A STUDY OF MOLECULAR COMPOUND FORMATION BETWEEN DINITROGEN TETROXIDE AND SOME SULFUR-CONTAINING LEWIS BASES

By

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES	iv
LIST OF FIGURES	v
INTRODUCTION	1
HISTORICAL REVIEW	5
EXPERIMENTAL PROCEDURES	15
RESULTS	35
DISCUSSION	50
SUMMARY	82
APPENDIXES	86
LITERATURE CITED	95

LIST OF TABLES

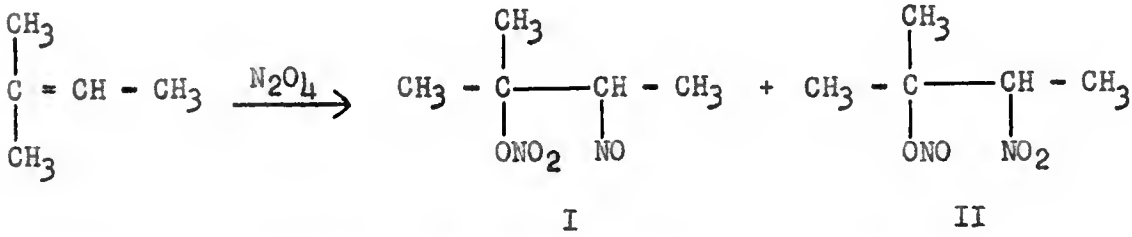
Table		Page
1.	Compounds Obtained Commercially	19
2.	System: Dimethyl Sulfide - Dinitrogen Tetroxide	36
3.	System: Bis-(chloromethyl) Sulfide - Dinitrogen Tetroxide	36
4.	System: Diethyl Sulfide - Dinitrogen Tetroxide	37
5.	System: Di-n-propyl Sulfide - Dinitrogen Tetroxide	38
6.	System: Di-n-butyl Sulfide - Dinitrogen Tetroxide	39
7.	System: Di-isoamyl Sulfide - Dinitrogen Tetroxide	40
8.	System: 1,4-Dithiane - Dinitrogen Tetroxide	41
9.	System: n-Butyl Ether - Dinitrogen Tetroxide	41
10.	System: Tetrahydropyran - Dinitrogen Tetroxide	42
11.	System: 1,4-Dioxane - Dinitrogen Tetroxide	42
12.	Freezing Point Depression	46
13.	Relative Polarizations of the Sulfide - Dinitrogen Tetroxide Addition Compounds at -60°	62
14.	Electric Moment Data for Some Sulfides and Ethers	63
15.	Apparent Stoichiometry of the Sulfide - Dinitrogen Tetroxide Compounds in Chloroform Solution from Dielectric Constant Measurements	73

LIST OF FIGURES

Figure		Page
1.	N_2O_4 Transfer Cell.	17
2.	Dielectric Constant Measuring Cell.	22
3.	Top of Dewar Flask.	24
4.	Apparatus for Preparation of Standard N_2O_4 Solutions. . . .	25
5.	Freezing Point Cell	30
6.	Glass Reaction Apparatus.	33
7.	Dimethyl Sulfide-Dinitrogen Tetroxide	43
8.	Diethyl Sulfide-Dinitrogen Tetroxide.	43
9.	Di-n-propyl Sulfide-Dinitrogen Tetroxide.	44
10.	Di-n-butyl Sulfide-Dinitrogen Tetroxide	44
11.	Di-isoamyl Sulfide-Dinitrogen Tetroxide	45

INTRODUCTION

It has been known for many years that the products of reactions between dinitrogen tetroxide and various organic compounds vary according to the solvent used. For example, in the absence of a solvent, or with petroleum ether, the following reaction leads to the formation of approximately equal amounts of products I and II.



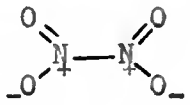
I II

However, if diethyl ether is used as a solvent for the reaction, product II is predominant. Similar differences in products are noted with other solvents (1).

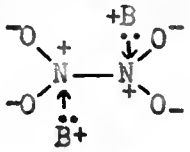
Since many common solvents are Lewis bases, and since dinitrogen tetroxide is a Lewis acid, it was reasonable to think that molecular addition compound formation between Lewis base solvents and dinitrogen tetroxide could perhaps be at least partially responsible for the observed facts.

During the last decade, there has been considerable work on the formation of addition compounds of dinitrogen tetroxide with

ethers, amines, and aromatic hydrocarbons and their derivatives. It has indeed been found that such molecules form addition compounds with dinitrogen tetroxide (2). From the work that has been done, it appears that dinitrogen tetroxide functions as a Lewis acid in one of two ways: (a) as an undissociated molecule,



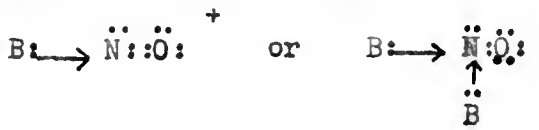
where one or two donor molecules, B:, can attack the nitrogen atoms,



or, (b) as an ionic species after dissociation,

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

where the NO^+ ion may be attacked by one or two donor molecules,



The nitrogen - nitrogen bond distance in dinitrogen tetroxide is 1.64 Å, as compared to 1.47 Å in hydrazine (2). Thus unusually long nitrogen-nitrogen bond distance in dinitrogen tetroxide affords a favorable steric condition for the increase in the coordination number of nitrogen from three to four when dinitrogen tetroxide forms addition compounds as in (a) above. Since donor molecules may approach either end of the dinitrogen tetroxide molecule, it is a simple matter for two donor molecules to unite with one molecule of dinitrogen

tetroxide when the addition compound contains dinitrogen tetroxide in molecular form. It is to be expected, then, that addition compounds in which the undissociated molecule of dinitrogen tetroxide functions as a Lewis acid will usually show a ratio of two moles of Lewis base to one mole of dinitrogen tetroxide.

If, however, dinitrogen tetroxide first ionizes before accepting electrons, as in (b) above, the situation is altered. Since only the NO^+ ion can accept electron pairs from Lewis bases, steric considerations strongly suggest that a 1:1 mole ratio for addition compounds should lead to greater stability than a ratio of two moles of Lewis base per mole of dinitrogen tetroxide. Likewise, electronic considerations indicate much greater stability for a 1:1 mole ratio. Thus it is to be expected that addition compounds in which dinitrogen tetroxide functions as a Lewis acid after first dissociating into NO^+ and NO_3^- ions will usually show a mole ratio of 1:1.

In an effort to elucidate further the formation of addition compounds of dinitrogen tetroxide with Lewis bases, the present work was undertaken. The addition compounds of ethers, amines, and some aromatic electron donor systems having been fairly well investigated, it was decided to extend the investigation to some aliphatic and alicyclic sulfides.

The choice of the sulfides was made for several reasons: first, the ether complexes had been characterized, and it was desirable to compare them with the addition compounds where the next member of

the oxygen family acts as the donor atom; second, the influence of the relatively large size of the sulfur atom was of interest; and third, information was sought concerning the mode of reaction, whether compound formation would occur as in (a) above or by an ionic mechanism such as (b) above. There were strong indications from previous work that some type of compound was formed between aliphatic sulfides and dinitrogen tetroxide.

It was indeed found that some sulfides do form addition compounds with dinitrogen tetroxide. These sulfide addition compounds, though relatively stable solids at low temperatures, oxidize immediately upon melting, thus making impossible the construction of phase diagrams. The method of study involved measurement of the change in dielectric constant in chloroform when solutions of dinitrogen tetroxide and the various sulfides were mixed in varying molar proportions. Dielectric constant measurements were used because they are easily made on systems at low temperatures and because they give an insight into the electrical properties of the systems.

HISTORICAL REVIEW

Physical Properties of Dinitrogen Tetroxide. Dinitrogen tetroxide freezes at -11.5°, and boils at 21.2°. It has a specific conductivity of 1.3×10^{-12} $ohm^{-1}cm^{-1}$ at 17° (3), a dielectric constant of 2.42 at 18°, which shows little variation with temperature (4), and a dipole moment equal to or nearly equal to zero for both liquid and gaseous phases (5).

Addition Compounds of Dinitrogen Tetroxide with Ethers. Addition compounds between dinitrogen tetroxide and the following ethers have been studied by construction of phase diagrams: ethyl ether, tetrahydrofuran, tetrahydropyran, 1,4-dioxane, β-β'-dichloroethyl ether (6), n-propyl ether, isopropyl ether, n-butyl ether, t-butyl ether, ethylene glycol ethyl ether, 1,3-dioxane, trioxane, perfluorotetrahydrofuran, α-methyltetrahydrofuran (7), trimethylene oxide, 2,5-dimethyltetrahydrofuran, and 1,3-dioxolane (8). Most of these molecules give addition compounds with a 2:1 mole ratio of ether to dinitrogen tetroxide. A few, particularly some cyclic ethers, are capable of forming 1:1 addition compounds. The system 1,3-dioxolane-dinitrogen tetroxide shows a mole ratio of two moles of ether to three moles of dinitrogen tetroxide.

β-β'-dichloroethyl ether, perfluorotetrahydrofuran, and

t-butyl ether do not form addition compounds with dinitrogen tetroxide. The presence of the highly electronegative groups on the former two molecules apparently decreases the basic strength of the oxygen atom so that no electron donation can occur. The failure of the latter molecule to form an addition compound is presumably caused by steric hindrance.

The usual stoichiometry of the ether addition compounds is 2:1 for ether to dinitrogen tetroxide. The compounds are white solids. Magnetic susceptibility data show the addition compounds to be diamagnetic. The absence of nitrogen dioxide radicals is clearly indicated since nitrogen dioxide radicals are brown in color and are paramagnetic. The characteristics of the ultra-violet spectra of these compounds show that ionic species like NO^+, NO_3^-, NO_2^+, or NO_2^- are absent. These facts indicate strongly that the addition compounds are of the molecular type. That is, dinitrogen tetroxide apparently functions as a Lewis acid while retaining its molecular identity (2).

Dinitrogen tetroxide and 1,4-dioxane form an addition compound where they are in a mole ratio of 1:1. This compound has a melting point of 45°, which is far above the melting points of any of the other ether-dinitrogen tetroxide addition compounds. The reason for this unusual stability lies in the fact that a small activation energy suffices to convert 1,4-dioxane from its more usual "chair" form to the "boat" form. In the "boat" form, the two oxygen atoms approach each other closely enough to donate electrons to both nitrogen

atoms in a single molecule of dinitrogen tetroxide. A cyclic structure results which accounts for the 1:1 stoichiometry. The compactness of the structure apparently allows favorable packing in the crystal lattice and leads to the relatively high melting point. With 1,3-dioxane this same phenomenon is observed, though the steric factors are not as favorable as with 1,4-dioxane. The melting point of the 1,3-dioxane addition compound is 2°, which is still far above most of the ether-dinitrogen tetroxide addition compounds. The fact that tetrahydrofuran and trimethylene oxide can also form 1:1 addition compounds remains unexplained. These molecules have but one basic center, so that no cyclization can occur as with the dioxanes. The explanation for the 2:3 mole ratio of 1,3-dioxolane to dinitrogen tetroxide is not known.

Addition Compounds of Dinitrogen Tetroxide with Amines.

Addition compounds between dinitrogen tetroxide and the following tertiary amines have been studied: pyridine, quinoline, isoquinoline, α-picoline, γ-picoline, acridine, 2,6-lutidine, 2-methylquinoline (9), triethylamine (9), (10), trimethylamine, dimethylmesidine, dimethylaniline, and N-methyldiphenylamine (10). These compounds are yellow or red crystalline solids at low temperatures and are analogous to complexes with nitrosyl chloride, with respect to ultra-violet spectra. Since such addition compounds with nitrosyl chloride increase the conductivity of solvents in which they are dissolved (10), (11), it is felt that they are ionic. By analogy, it is assumed that such

complexes of dinitrogen tetroxide are also ionic. In support of this idea is the fact that the solid complexes of dinitrogen tetroxide have very low solubilities in ethers and hydrocarbons, but are more soluble in more polar solvents like chlorinated hydrocarbons. If dinitrogen tetroxide does dissociate into NO^+ and NO_3^- ions, it would be reasonable to expect 1:1 addition compounds to predominate. It is found that the 1:1 type addition compound is usually formed for tertiary amines and dinitrogen tetroxide, though a 2:1 mole ratio of amine to dinitrogen tetroxide is also sometimes formed with heterocyclic amines. Pyridine gave a mole ratio of 2:3 for pyridine to dinitrogen tetroxide, as well as the more usual ratios of 1:1 and 2:1.

It has been suggested that addition compounds with strong electron donors such as the aliphatic tertiary amines exist as ionic compounds in both the solid and liquid state, whereas the weaker electron-donating heterocyclic amines give molecular compounds in the solid state, but undergo dissociation to some extent to give some of the ionic type compound in solution (12). Sterically hindered 2,6-lutidine and 2-methylquinoline give no compounds with dinitrogen tetroxide. When a great excess of dinitrogen tetroxide is added to aliphatic tertiary amines, unstable solid compounds result which contain very high mole ratios of dinitrogen tetroxide to amine.

Compounds with Other Oxygen-Containing Lewis Bases. Other oxygen-containing Lewis bases which have been studied include the following: dimethyl nitrosamine, diethyl nitrosamine, methyl phenyl

nitrosamine, ethyl phenyl nitrosamine, pentamethylene nitrosamine, methyl phenyl ketone, acetic acid, ethyl benzoate, acetone, benzaldehyde (12), ethyl acetate, benzophenone, and acetic anhydride (13). All give addition compounds with a mole ratio of Lewis base to dinitrogen tetroxide of 2:1, except benzophenone and acetic anhydride which also give 1:1 addition compounds, benzaldehyde, which gives only a 1:1 compound, and pentamethylene nitrosamine which gives 1:1 and 3:1 compounds, but no 2:1 compound. The usual mole ratio of 2:1 of nitrosamine to dinitrogen tetroxide indicates that in the solid phase at least, these compounds are perhaps molecular in character. However, solutions of diethyl nitrosamine in liquid dinitrogen tetroxide of the 2:1 ratio at 0° have a specific conductivity of 3.5×10^{-4} ohm^{-1} cm^{-1} (14), indicating considerable ionic dissociation of the nitrosamine addition compounds in solution, at this temperature.

The appearance of 1:1 addition compounds with benzophenone and benzaldehyde, both of which would have only small donating power through the oxygen atoms, can be explained on the basis of the fact that π orbitals of the aromatic rings overlap with vacant p orbitals on the nitrogen atoms in dinitrogen tetroxide. Support is given this idea by the fact that 1:1 compounds are formed between dinitrogen tetroxide and the following aromatic compounds: benzene, toluene, mesitylene, tetrahydronaphthalene, phenyl cyanide, benzyl cyanide, nitrobenzene (12), and p-tolyl cyanide (13). Most of these addition compounds are either orange or red. Dinitrogen tetroxide forms no

solid phase compounds with p-xylene, cyclohexane, chlorobenzene, or bromobenzene, although solutions of p-xylene in dinitrogen tetroxide at -20° have a deep red-brown color (12).

Acetonitrile and β-chloropropionitrile give solid phase compounds with dinitrogen tetroxide of the 2:1 type, though a 1:1 compound is also formed with acetonitrile (12).

Structures of the Dinitrogen Tetroxide Addition Compounds. Nitrosyl chloride usually functions as a Lewis acid after dissociation into NO^+ and Cl^- ions. The NO^+ ion can accept electrons from Lewis bases. Nitrosyl chloride does not form solid phase compounds with benzene, 1,4-dioxane, phenyl cyanide, or pyridine (12). This fact lends support to the belief that the addition compounds which dinitrogen tetroxide does form with these substances are primarily molecular rather than ionic.

The melting points of the various addition compounds correlate approximately with the proposed structure type. Ionic type addition compounds have higher melting points than molecular types although the melting points of both types, as a rule, are somewhat below 0°. The most notable exception to this generality is the very stable cyclic 1,4-dioxane-dinitrogen tetroxide molecular type addition compound.

In light of all the evidence concerning the above dinitrogen tetroxide addition compounds, it is reasonable to assume that in solution, the following equilibria exist:

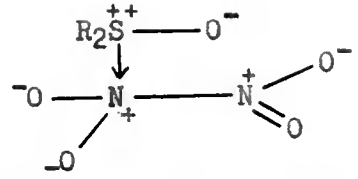
$$(B_nNO^+)(NO_3^-) \rightleftharpoons nB + N_2O_4 \rightleftharpoons N_2O_4 \cdot nB$$

In the case of the strongest donors, such as aliphatic tertiary amines, the equilibrium is shifted considerably to the ionic side, even in the solid state. With somewhat weaker doners, like nitrosamines or heterocyclic amines, the solid compounds are predominately molecular. In solution, however, some ionic dissociation probably occurs. With the weak donors, like the ethers or aromatic hydrocarbons, the equilibrium probably lies almost totally to the right, both in solution and in the solid state.

Classification of Addition Compounds of Dinitrogen Tetroxide with Electron Donors. Donor molecules with their unshared pairs of electrons in an s or p orbital, or some hybrid of these, have been called "onium donors," while donors with available electrons in a molecular orbital have been called "π donors." There arise four possible general classifications for the dinitrogen tetroxide addition compounds on the basis of the type of donor molecule: (a) molecular compounds with "onium donors," like the ethers; (b) ionic compounds with "onium donors," like the tertiary amines; (c) molecular compounds with "π donors," like the aromatic hydrocarbons; (d) ionic compounds with "π donors," of which type none have been observed (12), (2). There are, of course, overlapping cases such as the heterocyclic amines, which are intermediate between types (a) and (b) in solution, but shift to type (a) to a large extent in the solid phase.

Prior Work with Dinitrogen Tetroxide and Sulfur-Containing Lewis Bases. The first work with aliphatic sulfides and dinitrogen tetroxide was reported by Addison and Sheldon in 1956 (15). These workers found that dinitrogen tetroxide and aliphatic sulfides give red solids at temperatures near -70°, but that the red solids melt with immediate oxidation-reduction a little above this temperature. The product of the oxidation was found to be the corresponding sulfoxide, in almost quantitative yield. None of the corresponding sulfones were found as products. This fact suggests that dinitrogen tetroxide and the aliphatic sulfoxides form stable compounds which inhibit further oxidation of the sulfur. Indeed, it was found that dimethyl sulfoxide, diethyl sulfoxide, and di-n-propyl sulfoxide all give solid compounds with dinitrogen tetroxide, which have a 1:1 stoichiometry. Di-iso-propyl sulfoxide and dinitrogen tetroxide give a 2:1 compound as well as a 1:1 compound. All of these addition compounds are fairly stable, with melting points of 38°, 14°, and 20° for the former compounds, respectively, while that for the 2:1 di-isopropyl sulfoxide-dinitrogen tetroxide compound is -3° and that for the 1:1 compound, -10°.

Addison and Sheldon further found that diethyl sulfone gives no compound with dinitrogen tetroxide. The conclusion they drew is that electron donation occurs primarily from the sulfur atom rather than from the sulfoxide oxygen atom. The compounds were formulated as molecular in character; the 1:1 stoichiometry is explained on the basis of sulfoxide oxygen participation with the other nitrogen atom.



The existence of a 2:1 compound with di-isopropyl sulfoxide may be caused by steric factors which place the sulfoxide oxygen atom at too great a distance from the nitrogen atom for interaction. If such is the case, the second nitrogen atom would then be free to accept a pair of electrons from the sulfur atom of another sulfoxide molecule.

Job's Method of Continuous Variations. If some physical property which is specific to an addition compound is measured as a function of the mole ratio of the components of that compound, keeping total moles of components constant, it is easily shown[1] that a maximum or a minimum in the property should result when the mole ratio of the components corresponds to that of the compound. The usefulness of this fact was first realized by P. Job (16), and the method is now usually referred to as "Job's method of continuous variations." Any convenient physical property may be used, but it should be specific to the compound under study, or at least the contribution to the property by the individual components must be known. Spectrophotometric studies (17), (18), (19) are usually used in "Job's method," but other properties have also been used, for example, conductance (20).

When spectrophotometric analysis is employed, the usual procedure is to pick a suitable wavelength and measure optical density

[1]See Appendix I.

as a function of mole ratio of components, keeping the total number of moles constant. The difference between the observed optical density and the sum of the optical densities of the individual components in solution, had there been no interaction, is calculated. This difference is then plotted as a function of the mole ratio of the components, and a maximum indicates a compound of the formula indicated by the mole ratio of components at that point.

There are complications when more than one compound is formed. It has been shown (21) that when two compounds are formed, the physical property first reaches a maximum at a mole ratio which is below the actual mole ratio of the first compound, while the physical property reaches a second maximum at a mole ratio which is above the actual mole ratio of the second compound. The displacements are usually small, however, and introduce little error if the mole ratios of the two compounds are not close to each other.

Dielectric constant measurements have been used to study the formation of molecular addition compounds. For example, McCusker, et al. (22), (23), (24) measured the dielectric constants of solutions of various inorganic halides in dioxane. They did not, however, use the variations method in interpreting their results. Apparently, dielectric constant has not previously been used as the physical property for a variations study.

EXPERIMENTAL PROCEDURES

Methods of Analysis of Sulfide-Dinitrogen Tetroxide Systems. The primary method of analysis of the aliphatic and alicyclic sulfide-dinitrogen tetroxide systems employed in this work was that of "Job's method of continuous variations" using dielectric constant as the physical property measured. Chloroform was used as the solvent. A few ether-dinitrogen tetroxide systems in chloroform were also studied using this method.

Cryoscopic measurements were made on two of the more stable sulfide addition compounds in chloroform solutions in order to get a measure of the degree of dissociation of the compounds.

Solubilities of the addition compounds in several solvents besides chloroform were determined.

Finally, the oxidation of dithiane and trithiane by dinitrogen tetroxide was investigated.

Purification of Materials. Dinitrogen tetroxide was prepared by condensation of commercial nitrogen dioxide. Traces of nitric oxide are usually present in commercial nitrogen dioxide. Nitric oxide combines with nitrogen dioxide to form dinitrogen trioxide, which is deep blue in color in the liquid or solid state (B. P. 5°). The presence of an impurity from this source in nitrogen dioxide is

thus easily detected by condensing the nitrogen dioxide to liquid or solid dinitrogen tetroxide. Any blue or greenish-blue coloration indicates the presence of dinitrogen trioxide. At first, the dinitrogen trioxide was converted into dinitrogen tetroxide by bubbling oxygen gas through the impure dinitrogen tetroxide at 0° until the greenish solution became brown. However, it was later found that the traces of nitric oxide could be removed by passing the gas at a moderate rate from the cylinder directly through a short glass tube (10 cm. long and 1.5 cm. in diameter) filled with phosphorus (V) oxide and sand. The nitrogen dioxide was condensed to snow white solid dinitrogen tetroxide in a glass trap cooled by a chloroform-carbon tetrachloride-dry ice mixture. Freezing point measurements indicated that the dinitrogen tetroxide obtained from this treatment was quite pure. Exactly how the purification was effected by the phosphorus (V) oxide and sand is unexplained. Complete drying of the dinitrogen tetroxide was obtained by warming the trap to room temperature and slowly distilling the dinitrogen tetroxide through a longer glass tube (40 cm. long and 2 cm. in diameter) filled with phosphorus (V) oxide and sand into a transfer cell (Fig. 1) cooled by the dry ice mixture. The transfer cell was kept in a refrigerator at about 5° until the dinitrogen tetroxide was needed. The pure dinitrogen tetroxide could be conveniently stored for several months in this manner. Glass apparatus was used as far as possible in handling the dinitrogen tetroxide, but some connections were made with thin-walled Teflon

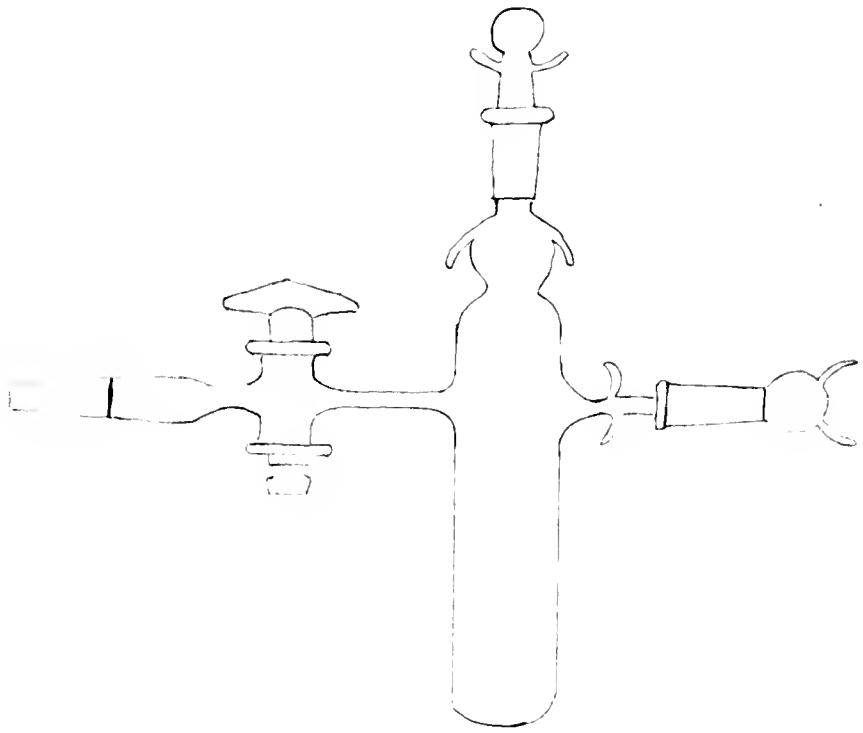


Fig. 1 - N_2O_4 Transfer Cell

tubing. The Teflon showed no signs of decomposition after two years of use.

The aliphatic sulfides investigated in this work were: bis-(chloromethyl) sulfide, dimethyl sulfide, diethyl sulfide, di-n-propyl sulfide, di-n-butyl sulfide, and di-isoamyl sulfide. The alicyclic sulfides studied were 1,4-dithiane and trithiane. The following ethers were also investigated: 1,4-dioxane, n-butyl ether, and tetrahydropyran. All of these substances with the exception of dithiane were obtained from commercial sources. The liquids were dried and distilled; the constant boiling middle cut was retained. A list of the compounds obtained commercially is found in Table 1.

Dithiane was synthesized by a method similar to one reported in the literature by Masson (25), in which dithiane is prepared by the reaction of potassium sulfide with ethylene dibromide in alcohol solution. A mixture of 600 ml. of 95 per cent ethanol and 250 g. of potassium hydroxide was saturated with hydrogen sulfide gas. This mixture was then placed in a large round bottom flask fitted with dropping funnel, stirrer, and reflux condenser. With rapid stirring, 282 g. of ethylene dibromide was added dropwise at a rate sufficient to maintain gentle reflux, the heat of reaction being sufficient to accomplish this. After all the ethylene dibromide had been added, the mixture was warmed to maintain a gentle reflux for two more hours. At the end of that time, the mixture, which was a white paste, was steam distilled. About 500 ml. of a clear, colorless alcoholic

TABLE 1

COMPOUNDS OBTAINED COMMERCIALLY

Substance	Source*	Drying Agent	B.P. of cut (uncorr.)	Lit. B.P.
$ClCH_2SCH_2Cl$	S	Anhyd. $CaCl_2$	156-7°	156°
CH_3SCH_3	CZ	Na	37.2°	37.1-.2°
$C_2H_5SC_2H_5$	D	Anhyd. $CaCl_2$	90.3°	92.1°
$C_3H_7SC_3H_7$	E	Na	140-1°	142-3°
$C_4H_9SC_4H_9$	E	Anhyd. $CaCl_2$	185-6°	182°
$C_5H_{11}SC_5H_{11}$	E	Anhyd. $CaCl_2$	216-7°	216°
$SCH_2SCH_2SCH_2$	E	-	(M.P. 216-8°)	(M.P. 216°)
$OCH_2CH_2OCH_2CH_2$	C	Na	101°	101.4°
$C_4H_9OC_4H_9$	C	Na	140°	142.4°
$OCH_2CH_2CH_2CH_2CH_2$	EN	Na	87.5-.6°	88°

*S - Stauffer Chemical Co.

CZ - Crown Zellerbach Corporation

E - Eastman Chemicals

C - Carbide and Carbon Chemicals Co.

EN - Eastern Chemical Co.

forerun was obtained. It was diluted to two liters with water and placed in a refrigerator. Solid dithiane crystallized in a short time. Continued steam distillation of the reaction mixture carried over solid dithiane. The total amount of dithiane produced was about 18 g. The yield was only 20 per cent, but the product was of high purity. One recrystallization from 95 per cent ethanol produced a snow white, almost odorless product. M. P. 111.2-112.0°, Lit. 111-12°.

Chloroform of U.S.P. grade was obtained from Fisher Chemical Company. It was allowed to stand for at least a week over anhydrous calcium chloride. Following this treatment, it was fractionated in a 121 cm. heated column, packed with glass helices, at a reflux ratio of about 50:1. The alcohol azeotrope distilled at 59°. When the head temperature became 61°, the reflux ratio was decreased and the chloroform collected. The 61° fraction was immediately fractionated in an 87 cm. heated column, packed with small saddles, at a reflux ratio of about 5:1. After removal of a small forerun, chloroform boiling at 61.2-.3° was collected. The literature value is 61.2°. Since chloroform which has had the alcohol removed is susceptible to oxidation, the fractionations were carried out immediately prior to using the chloroform.

Dielectric Constant Measurements. The dielectric constants of the various solutions of the addition compounds were measured by the heterodyne beat method. The instrument used consists essentially of a fixed quartz crystal oscillator operating at 250 kilocycles in

conjunction with a vacuum tube oscillator of variable frequency controlled by the adjustment of a precision condenser. The resistance and inductance remain substantially constant. A one kilocycle tuning fork is beat against the difference between the fixed and variable oscillators. An oscilloscope was used so that visual as well as audible means were employed to determine when the constant difference of one kilocycle obtained between the quartz and variable oscillators. After such balance of the system was obtained without the measuring cell containing the solution under study, the cell was connected in parallel with the precision condenser and balance then re-established by manipulation of the precision condenser. The difference in capacitance to the nearest tenth of a micro-micro farad between the balanced system without the measuring cell and the balanced system with the measuring cell was read directly from the precision condenser. This difference gave the capacitance of the measuring cell. The dielectric constants of the solutions were calculated by dividing the capacitance of the measuring cell with the particular solution as the dielectric by the capacitance of the cell with dry air between the plates (26).

The measuring cell (Fig. 2) used in these studies was obtained from J. C. Balsbaugh, Marshfield Hills, Massachusetts, type 2TN50. It was constructed of pyrex type glass. The capacitance of the glass and wire leads was obtained by measuring the dielectric constant of a constant boiling fraction of Eastman spectral grade iso-octane, at

-60°. A temperature correction to the dielectric constant of isooctane was applied by the relation:

$$\epsilon_t = 1.940 - 0.00142(t - 20) \quad (27)$$

The temperature of the measuring cell was controlled by means of a Dewar flask fitted with a calibrated toluene-in-glass thermometer (Fig. 3). A chloroform and carbon tetrachloride solution was cooled to the temperature at which the measurements were to be taken and small pieces of dry ice added from time to time as necessary to maintain the low temperature. Most of the measurements were made at -60°.

Standard solutions of dinitrogen tetroxide in chloroform were prepared using an all glass apparatus (Fig. 4). Receiver A was filled with approximately 15 ml. of chloroform. With ball joint B sealed, the entire receiver was weighed to the nearest milligram. The female bridge was then attached to ball joint B so as to connect the dinitrogen tetroxide transfer cell. With stopcock C open and stopcock D closed, receiver A was cooled to -50° to -60°. Stopcock D was then opened and dinitrogen tetroxide allowed to distill into receiver A. The rate of distillation could be controlled by regulating the height of the cooling bath and warming the dinitrogen tetroxide transfer cell with the hand. From time to time, stopcocks C and D were closed and the transfer cell was removed and weighed in order to get an approximate measure of the dinitrogen tetroxide which had distilled. When the desired amount, plus a small excess, had distilled, the

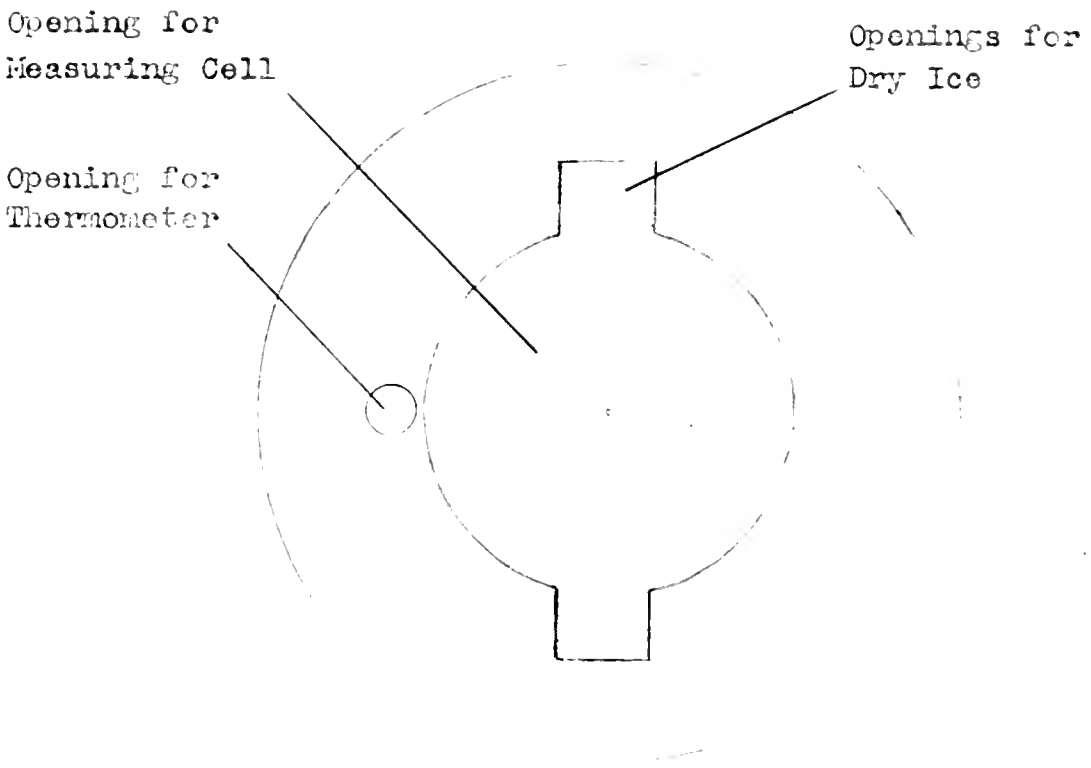


Fig. 3 - Top of Dewar Flask

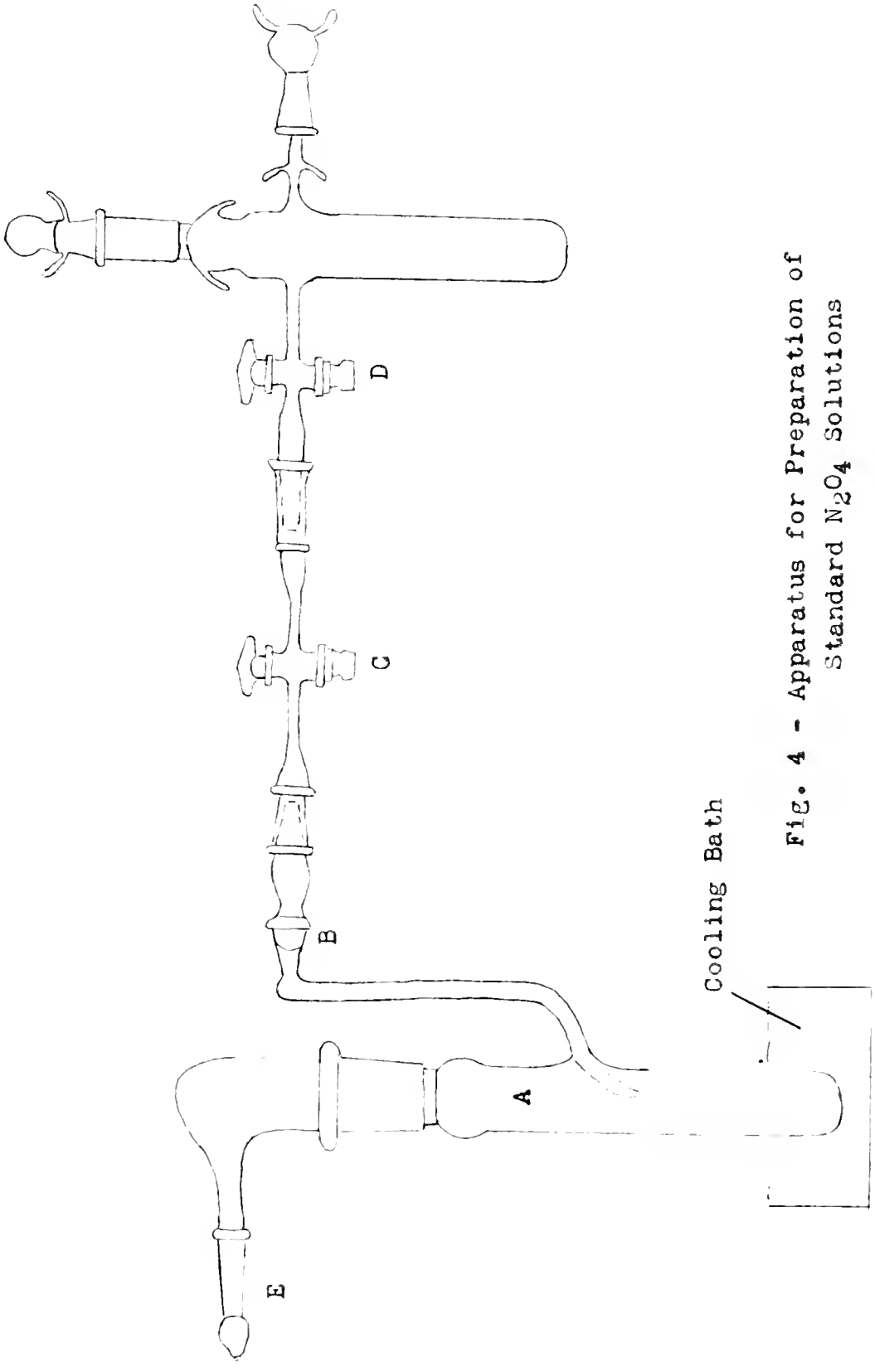


Fig. 4 - Apparatus for Preparation of Standard N_2O_4 Solutions

cooling bath was removed, stopcock D closed, and the transfer cell removed. As the receiver A warmed to room temperature, some of the dinitrogen tetroxide would unavoidably be lost by volitilization. From experience, this loss could be estimated and the necessary excess added as mentioned. After the receiver A had warmed to room temperature, ball joint B was again sealed and the receiver weighed to the nearest milligram. By difference, the weight of dinitrogen tetroxide added to the chloroform was obtained. Cap E was then removed and the standard taper male joint inserted into a volumetric flask containing about 50 ml. of chloroform. By careful pouring, the dinitrogen tetroxide-chloroform solution in receiver A was transferred to the volumetric flask. The receiver was rinsed several times with chloroform and these washings added to the volumetric flask. The volumetric flask was then diluted to the mark with chloroform, at room temperature. The standard sulfide and ether solutions in chloroform were prepared by directly weighing the components of the solutions.

The concentrations of solutions employed were about 0.05 - 0.06M since, at such small concentrations, the dielectric constant of the separate dinitrogen tetroxide and sulfide and ether solutions at -60° was essentially that of pure chloroform at -60°. Also, at these concentrations, loss by evaporation of dinitrogen tetroxide is slight and was shown to introduce only small error.[2]

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[2]See Appendix II.

Provided volumes are additive, the varying of mole ratios of the components of a compound, as required in the method of continuous variation, may be accomplished by varying the relative volumes of solutions which contain each of the components at equal concentrations while always holding the total volume constant (16), (28). This method was employed since volumes certainly are substantially additive at a concentration of 0.06M.

Total volume in the cell was held at 50 ml., measured at room temperature. At -60°, the volume was approximately 45 ml. The observed volume contraction is in good agreement with the expected contraction for pure chloroform at the same temperature, which reinforces the assumption of additivity of volumes. A typical experiment was carried out as follows: 20 ml. of a 0.06M solution of the sulfide was pipetted into the glass measuring cell, and the cell was then fitted with a drying tube filled with phosphorus (V) oxide and sand. Next, 30 ml. of a 0.06M solution of dinitrogen tetroxide was pipetted into a cylinder bent at the top and equipped with a male joint which would fit into the dielectric constant measuring cell. This cylinder was likewise fitted with a drying tube filled with phosphorus (V) oxide and sand. Both the measuring cell and the cylinder were then immersed in a cooling bath at -78° for about two minutes. At the end of this time, the drying tubes were removed, the cylinder was fitted into the measuring cell, and the cooled solutions were mixed. The cell, with the cylinder still attached, was then returned to the cooling bath

for a little longer and shaken occasionally to insure thorough mixing. In the case of the sulfide-dinitrogen tetroxide systems, the colorless solutions of the two components form a red solution upon mixing. Finally, the measuring cell, with the cylinder, was placed in the Dewar flask containing chloroform and the carbon tetrachloride at the temperature at which the measurement was to be made. The cylinder was then removed and the nickel condenser fitted into the measuring cell. The system was allowed to stand twenty minutes to establish temperature equilibrium. Small pieces of dry ice were added to the Dewar flask as necessary. At the end of twenty minutes, the capacitance of the cell was measured. Determination of the temperature of the solution in the cell immediately after taking the capacitance measurement in every case showed its temperature to be equal to that indicated by the thermometer in the cooling bath of the Dewar flask. Theoretical calculations[3] also predict that temperature equilibrium was reached. From experiments such as that just described, the dielectric constant of a solution in which the mole ratio of sulfide to dinitrogen tetroxide is 2:3 was obtained. The dielectric constants of solutions with other mole ratios were obtained in the same way by using different volume proportions; e.g., using 25 ml. of each solution would give data for a 1:1 mole ratio.

Measurements of Freezing Point Depression. The lowering of the freezing point of chloroform solutions of two of the more stable

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[3]See Appendix III.

sulfide addition compounds was measured. Using solutions in which the sulfide to dinitrogen tetroxide mole ratio was that as indicated for the addition compound by the dielectric constant studies, a calculation of the degree of dissociation of the addition compound was possible. The molal freezing point depression of chloroform was determined from solutions of known concentrations of dinitrogen tetroxide.

A variable range, variable zero Speedomax, Type G, Leeds and Northrup Recording Potentiometer fitted with a copper-constantan thermocouple was used to measure temperature. The freezing point cell (Fig. 5) was equipped with a thermocouple well filled with iso-octane to insure good thermal contact. The solutions were stirred constantly as the temperature was lowered in a chloroform-carbon tetrachloride-dry ice bath. The stirring was accomplished by a glass spiral, the top part of which was connected to a sealed glass tube containing an iron slug. A solenoid was placed around the upper part of the freezing point cell in such a manner that by alternate activation and deactivation, the stirrer was agitated. Alternate activation and deactivation of the solenoid was obtained by means of a small constant-speed motor which turned a split ring commutator on brushes in series with a rheostat which powered the solenoid.

Attempts to Isolate Solid Complexes. Many attempts were made to precipitate the sulfide-dinitrogen tetroxide addition compounds out of solution. The compounds are very soluble in chloroform, giving yellow-red to red solutions. They are also quite soluble in

ethyl ether, giving yellowish solutions. In ether solutions, they seem to be fairly susceptible to oxidation-reduction, the solutions often becoming greenish in color after a few minutes, even at -78°. The compounds are very soluble in acetone, giving colors similar to the chloroform solutions except darker. In hexane, yellow solutions result, though the compounds are only moderately soluble. At -78°, in hexane solutions, a tar-like substance settles out after a few hours. The color of this tar-like substance depends upon the concentrations of the dinitrogen tetroxide and sulfide solutions. When dilute solutions are mixed, the tar is brownish green, whereas with more concentrated solutions, the color is red. No well-defined crystalline solid could ever be isolated, however.

As soon as the temperature of any of these solutions is allowed to rise much above -50°, the solutions containing aliphatic sulfides and dinitrogen tetroxide turn green. Cooling does not restore the original color. If, however, trithiane or dithiane is used as the sulfide, warming the solution, even to room temperature, does not produce a green color, but simply the brown color of nitrogen dioxide. Brown fumes can be seen above the solution. Upon cooling these solutions to around -50°, the original purple to red color is restored. This reversible color change can be made to occur several times before oxidation-reduction renders the change impossible.

Numerous attempts were made to isolate pure solid addition compounds by adding a given sulfide to a large excess of dinitrogen

tetroxide at -50° to -55°. The solid mixture of addition compound and excess dinitrogen tetroxide was then subjected to reduced pressure in an attempt to remove the excess dinitrogen tetroxide, which has a vapor pressure in excess of one millimeter of mercury at -55°. The dry, red solids which result were hydrolyzed with a 0.5M NaOH in 50 per cent ethanol solution. Total nitrogen and sulfur analyses were obtained to determine mole ratios of addition compound constituents, assuming only dinitrogen tetroxide and the particular sulfide to be the components. No consistent results could be obtained. Relative excesses of dinitrogen tetroxide and length of vacuum applications were varied considerably in different experiments. Apparently the sulfide-dinitrogen tetroxide addition compounds are not stable at pressures around one millimeter of mercury, even at -50° to -55°.

Most of these experiments were carried out in a specially designed all-glass reaction apparatus (Fig. 6).

Oxidation of Dithiane and Trithiane by Dinitrogen Tetroxide. A large excess of dinitrogen tetroxide was distilled directly onto solid dithiane in the reaction apparatus. The temperature of the mixture was brought to 0° and held for about 12 hours. At the end of that time, the solution was blue with a white solid on the bottom of the container. Excess dinitrogen tetroxide was removed by vacuum. The solid residue decomposed at 225-30°. After recrystallization from 95 per cent ethanol, the resulting solid decomposed at 263-5°. Sub-

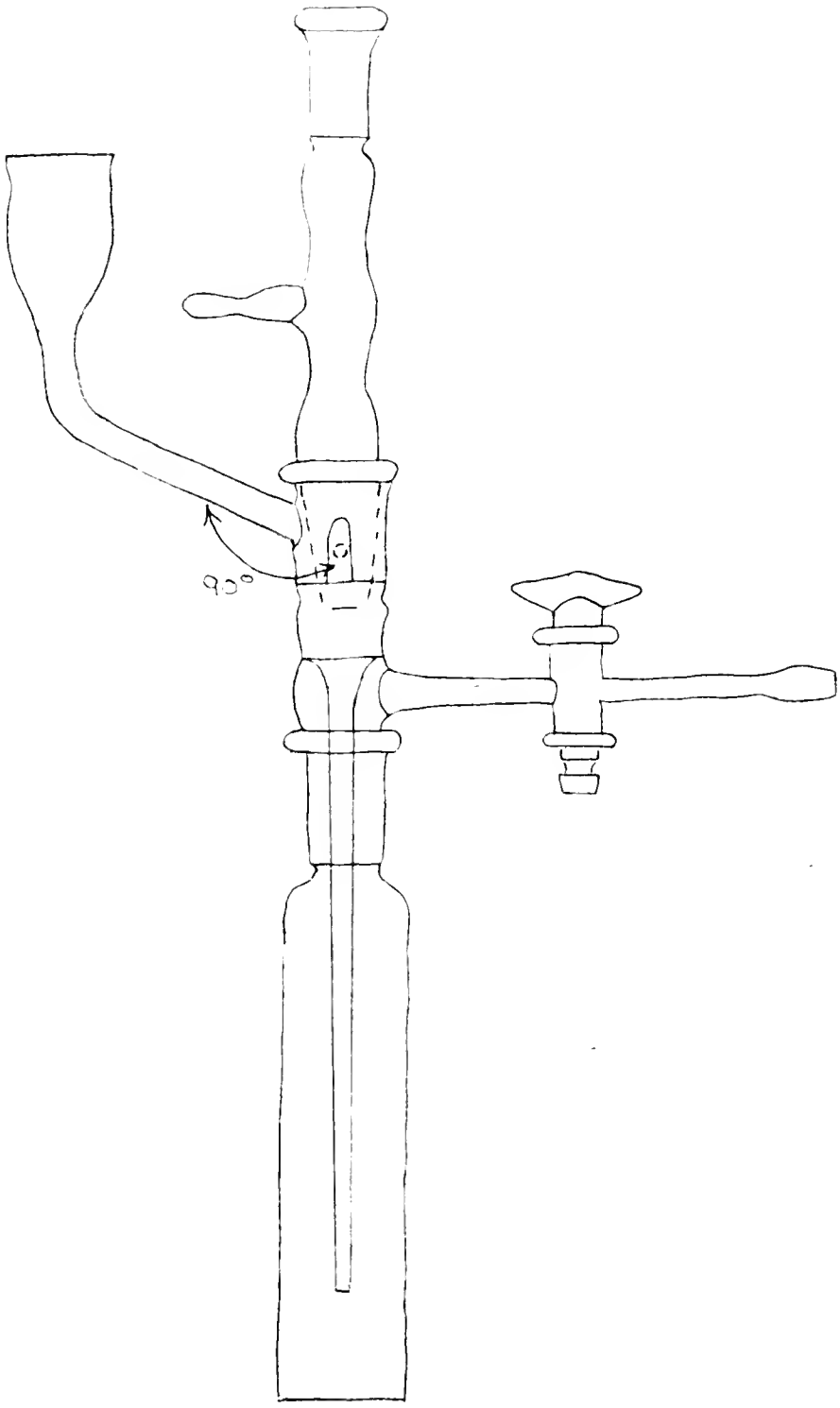


Fig. 6 - Glass Reaction Apparatus

limation of the solid which decomposed at 225-30°, gave another white solid, which, after recrystallization from 95 per cent ethanol, melted at 205-7°. It was found that addition of excess dinitrogen tetroxide at 0° for a few hours to the solid decomposing at 263-5°, followed by removal of excess dinitrogen tetroxide, reforms the white solid decomposing at 225-30°. Elementary analyses for nitrogen and sulfur were performed on these white solids. A quantitative carbon and hydrogen determination was made on the solid melting at 205-7°.

A similar treatment of trithiane with liquid dinitrogen tetroxide resulted in the formation of an amorphous, yellow solid, which was insoluble in all ordinary solvents. The substance contained some free sulfur, but no crystallization could be induced after extraction with carbon disulfide. Sublimation of the substance led to its complete decomposition with the production of gaseous products with foul sulfide-like odors.

RESULTS

Dielectric Constant Measurements. Results for all systems studied by means of measurement of their dielectric constants in chloroform solutions are presented in tables 2 through 11. Listed in these tables are the following: the temperature in degrees Centigrade, T, at which the measurement was made; the molarity, M, of both the sulfide and dinitrogen tetroxide solutions before mixing; the color of the solution after mixing, i.e., the color of the addition compound in solution; the volumes in milliliters of the sulfide and dinitrogen tetroxide solutions; the mole ratio of sulfide to dinitrogen tetroxide in the solution after mixing; and, finally, the dielectric constant, ϵ, of the solution.

For those sulfide-dinitrogen tetroxide systems which show a significant increase in dielectric constant over the dielectric constant of chloroform, and hence are amenable to analysis by Job's method of continuous variations, the data, for -60.0°, are also presented graphically in figures 7 through 11.

The dielectric constant of pure chloroform at -60° was found to be 6.75.

TABLE 2

SYSTEM: DIMETHYL SULFIDE - DINITROGEN TETROXIDE

T	M	Color	Mls. Sulfide Soln.	Mls. N_2O_4 Soln.	Mole Ratio Sulfide/N_2O_4	ϵ
-60.0°	0.062	Pale yellow	10.0	40.0	1:4	7.04
-60.0°	0.062	Light orange	15.0	35.0	1:2.3	7.13
-60.0°	0.062	Light orange	20.0	30.0	1:1.5	7.20
-60.0°	0.062	Light orange	25.0	25.0	1:1	7.27
-60.0°	0.062	Light orange	30.0	20.0	1:0.67	7.23
-60.0°	0.062	Light orange	35.0	15.0	1:0.43	7.19
-60.0°	0.062	Pale yellow	40.0	10.0	1:0.25	7.10
-56.0°	0.065	Light orange	25.0	25.0	1:1	6.95
-52.0°	0.065	Light orange	25.0	25.0	1:1	6.86

TABLE 3

SYSTEM: BIS-(CHLOROMETHYL) SULFIDE - DINITROGEN TETROXIDE

T	M	Color	Mls. Sulfide Soln.	Mls. N_2O_4 Soln.	Mole Ratio Sulfide/N_2O_4	ϵ
-60.0°	0.096	Colorless	10.0	40.0	1:4	6.76
-60.0°	0.096	Colorless	20.0	30.0	1:1.5	6.75
-60.0°	0.096	Colorless	25.0	25.0	1:1	6.74
-60.0°	0.096	Colorless	35.0	15.0	1:0.43	6.75

TABLE 4

SYSTEM: DIETHYL SULFIDE - DINITROGEN TETROXIDE

T	M	Color	Mls. Sulfide Soln.	Mls. N_2O_4 Soln.	Mole Ratio Sulfide/N_2O_4	ϵ
-60.0°	0.060	Pale orange-red	5.0	45.0	1:9	7.24
-60.0°	0.060	Orange-red	10.0	40.0	1:4	7.41
-60.0°	0.060	Orange-red	12.0	38.0	1:3.2	7.43
-60.0°	0.060	Orange-red	15.0	35.0	1:2.3	7.45
-60.0°	0.060	Orange-red	17.0	33.0	1:1.9	7.42
-60.0°	0.060	Orange-red	20.0	30.0	1:1.5	7.41
-60.0°	0.060	Orange-red	25.0	25.0	1:1	7.31
-60.0°	0.060	Orange-red	30.0	20.0	1:0.67	7.31
-60.0°	0.060	Pale red-orange	35.0	15.0	1:0.43	7.22

TABLE 5

SYSTEM: DI-n-PROPYL SULFIDE - DINITROGEN TETROXIDE

T	M	Color	Mls. Sulfide Soln.	Mls. N_2O_4 Soln.	Mole Ratio Sulfide/N_2O_4	ϵ
-60.0°	0.060	Orange	10.0	40.0	1:4	7.58
-60.0°	0.060	Red-orange	12.0	38.0	1:3.2	7.70
-60.0°	0.060	Red-orange	15.0	35.0	1:2.3	7.77
-60.0°	0.060	Red-orange	20.0	30.0	1:1.5	7.70
-60.0°	0.060	Orange-red	25.0	25.0	1:1	7.68
-60.0°	0.060	Orange-red	30.0	20.0	1:0.67	7.62
-60.0°	0.060	Orange	35.0	15.0	1:0.43	7.53
-60.0°	0.060	Pale orange	40.0	10.0	1:0.25	7.33

TABLE 6

SYSTEM: DI-n-BUTYL SULFIDE - DINITROGEN TETROXIDE

T	M	Color	Mls. Sulfide Soln.	Mls. N_2O_4 Soln.	Mole Ratio Sulfide/N_2O_4	ϵ
-60.0°	0.045	Orange-red	15.0	35.0	1:2.3	7.56
-60.0°	0.045	Orange-red	20.0	30.0	1:1.5	7.56
-60.0°	0.045	Orange-red	25.0	25.0	1:1	7.56
-60.0°	0.045	Orange-red	34.0	16.0	1:0.47	7.48
-60.0°	0.062	Dark orange-red	10.0	40.0	1:4	7.51
-60.0°	0.062	Dark orange-red	15.0	35.0	1:2.3	7.71
-60.0°	0.062	Dark orange-red	17.5	32.5	1:1.9	7.68
-60.0°	0.062	Dark orange-red	20.0	30.0	1:1.5	7.72
-60.0°	0.062	Dark orange-red	22.0	28.0	1:1.3	7.71
-60.0°	0.062	Dark orange-red	25.0	25.0	1:1	7.65
-60.0°	0.062	Orange-red	30.0	20.0	1:0.67	7.63
-60.0°	0.062	Orange-red	33.0	17.0	1:0.52	7.47
-60.0°	0.062	Red-orange	40.0	10.0	1:0.25	7.29
-56.0°	0.065	Dark orange-red	20.0	30.0	1:1.5	7.58
-52.5°	0.065	Dark orange-red	20.0	30.0	1:1.5	7.41

TABLE 7

SYSTEM: DI-ISOAMYL SULFIDE - DINITROGEN TETROXIDE

T	M	Color	Mls. Sulfide Soln.	Mls. N_2O_4 Soln.	Mole Ratio Sulfide/N_2O_4	ϵ
-60.0°	0.060	Orange-red	5.0	45.0	1:9	7.26
-60.0°	0.060	Dark orange-red	10.0	40.0	1:4	7.40
-60.0°	0.060	Dark orange-red	15.0	35.0	1:2.3	7.60
-60.0°	0.060	Dark orange-red	20.0	30.0	1:1.5	7.68
-60.0°	0.060	Dark orange-red	25.0	25.0	1:1	7.61
-60.0°	0.060	Orange-red	30.0	20.0	1:0.67	7.42
-60.0°	0.060	Red-orange	35.0	15.0	1:0.43	7.27
-60.0°	0.060	Red-orange	40.0	10.0	1:0.25	7.22
-60.0°	0.060	Yellow-orange	45.0	5.0	1:0.11	6.94

TABLE 8

SYSTEM: 1,4-DITHIANE - DINITROGEN TETROXIDE

T	M	Color*	Mls. Sulfide Soln.	Mls. N_2O_4 Soln.	Mole Ratio Sulfide/N_2O_4	ϵ
-60.0°	0.046	Pale yellow	1.0	49.0	1:49	6.84
-60.0°	0.046	Pale red-orange	5.0	45.0	1:9	6.86
-60.0°	0.046	Pale red-orange	10.0	40.0	1:4	6.82
-60.0°	0.046	Pale red-orange	15.0	35.0	1:2.3	6.79
-60.0°	0.046	Very pale orange-yellow	25.0	25.0	1:1	6.74
-60.0°	0.046	Very pale yellow	44.0	16.0	1:0.14	6.69
-60.0°	0.060	Very pale yellow	25.0	25.0	1:1	-

*There was an induction period of about a minute after mixing the colorless solutions before the color appeared as described.

TABLE 9

SYSTEM: n-BUTYL ETHER - DINITROGEN TETROXIDE

T	M	Color	Mls. Ether Soln.	Mls. N_2O_4 Soln.	Mole Ratio Ether/N_2O_4	ϵ
-60.0°	0.05	Colorless	15.0	35.0	1.2.3	6.82
-60.0°	0.05	Colorless	25.0	25.0	1:1	6.85
-60.0°	0.05	Colorless	35.0	15.0	1:0.43	6.82

TABLE 10

SYSTEM: TETRAHYDROPYRAN - DINITROGEN TETROXIDE

T	M	Color*	Mls. Ether Soln.	Mls. N_2O_4 Soln.	Mole Ratio Ether/N_2O_4	ϵ
-60.0°	0.057	Colorless	10.0	40.0	1:4	6.87
-60.0°	0.057	Colorless	15.0	35.0	1:2.3	6.89
-60.0°	0.057	Colorless	20.0	30.0	1:1.5	6.93
-60.0°	0.057	Colorless	25.0	25.0	1:1	6.93
-60.0°	0.057	Colorless	30.0	20.0	1:0.67	6.95
-60.0°	0.057	Colorless	33.0	17.0	1:0.52	6.90
-60.0°	0.057	Colorless	40.0	10.0	1:0.25	6.87
-60.0°	0.057	Colorless	45.0	5.0	1:0.11	6.85

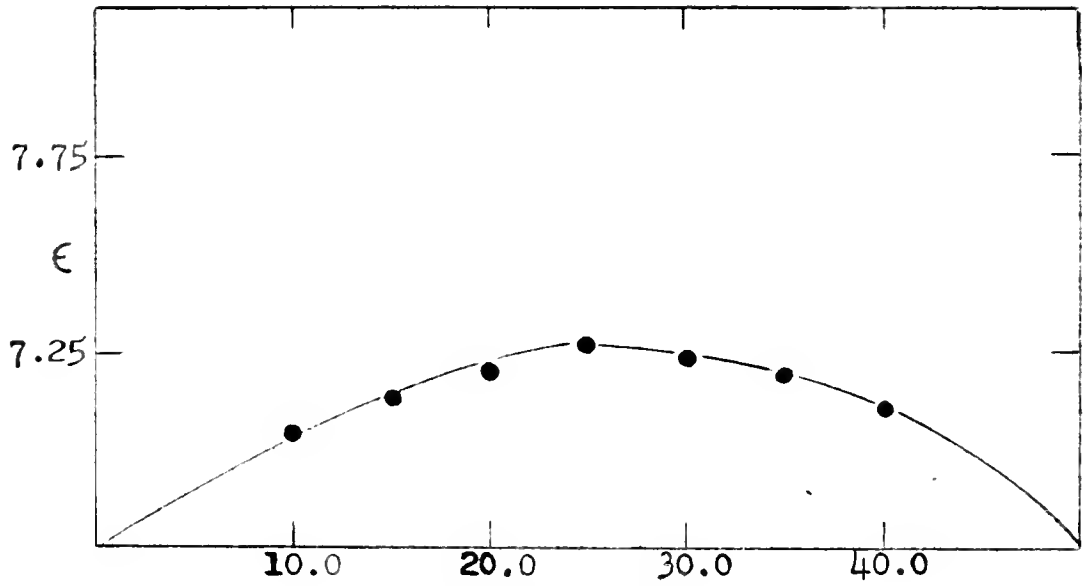
*At the end of the experiments, the solutions were very pale blue.

TABLE 11

SYSTEM: 1,4-DIOXANE - DINITROGEN TETROXIDE

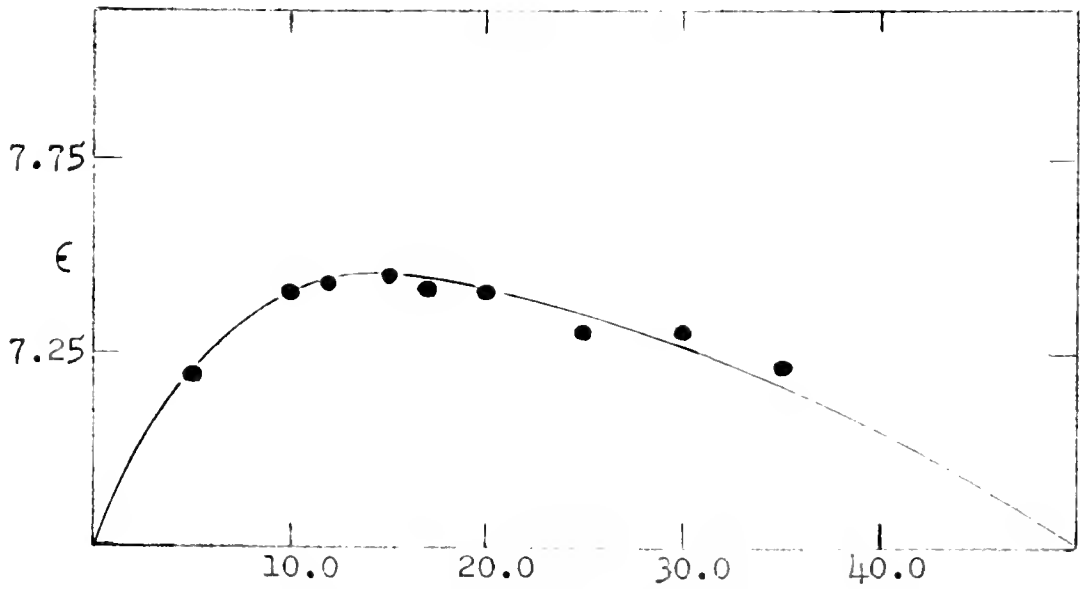
T	M	Color*	Mls. Ether Soln.	Mls. N_2O_4 Soln.	Mole Ratio Ether/N_2O_4	ϵ
-60.0°	0.056	Colorless	20.0	30.0	1:1.5	6.70
-60.0°	0.056	Colorless	25.0	25.0	1:1	6.69
-60.0°	0.056	Colorless	30.0	20.0	1:0.67	6.72

*At the end of the experiments, the solutions were extremely pale blue.



Mls. 0.062M Dimethyl sulfide

Fig. 7 - Dimethyl Sulfide-Dinitrogen Tetroxide



Mls. 0.060M Diethyl sulfide

Fig. 8 - Diethyl Sulfide-Dinitrogen Tetroxide

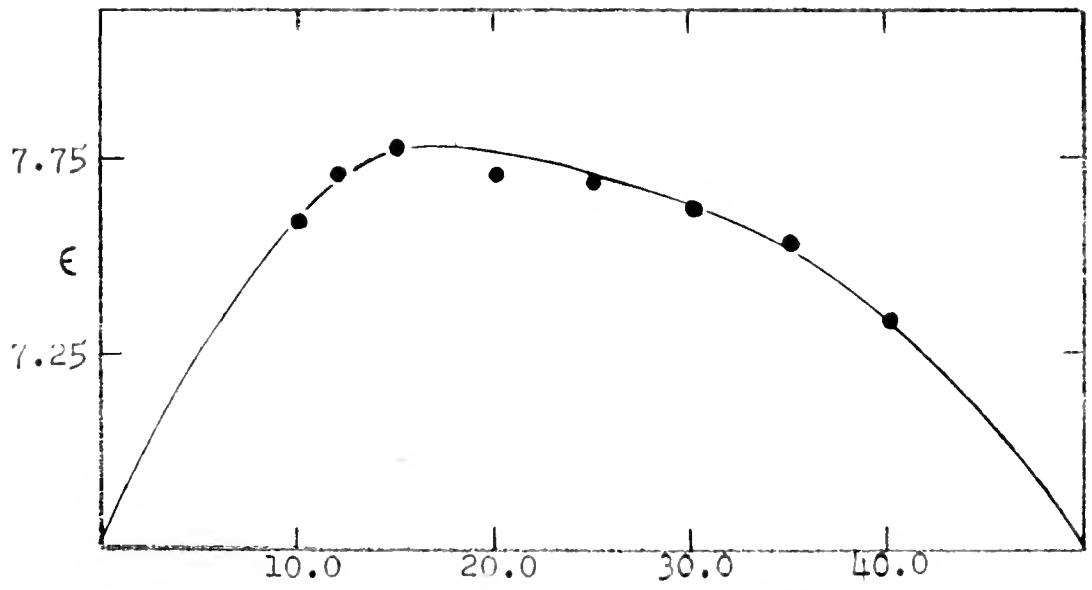


Fig. 9 - Di-n-propyl Sulfide-Dinitrogen Tetroxide

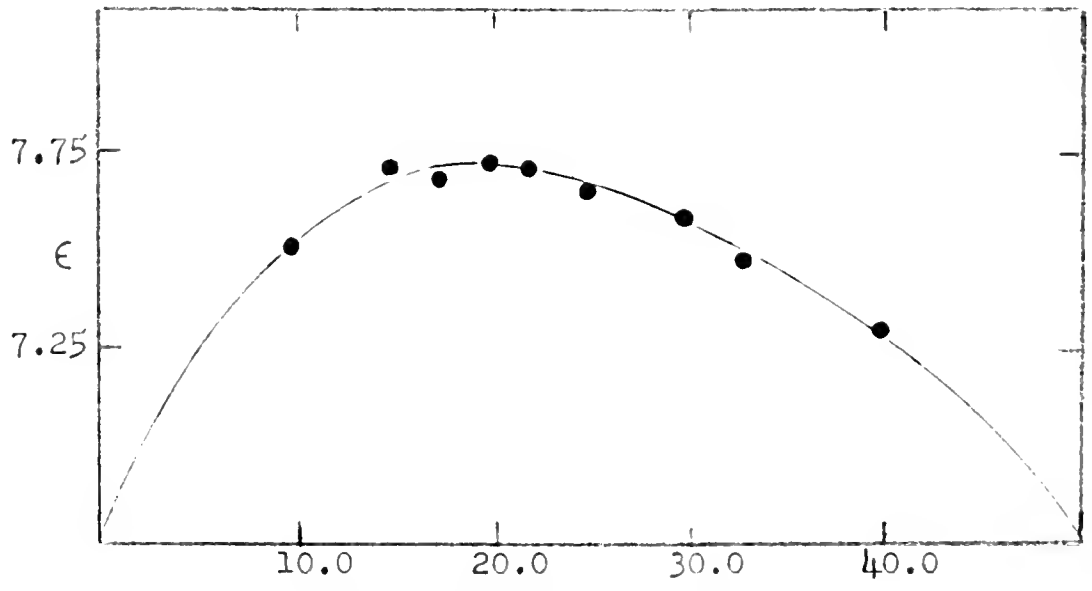


Fig. 10 - Di-n-butyl Sulfide-Dinitrogen Tetroxide

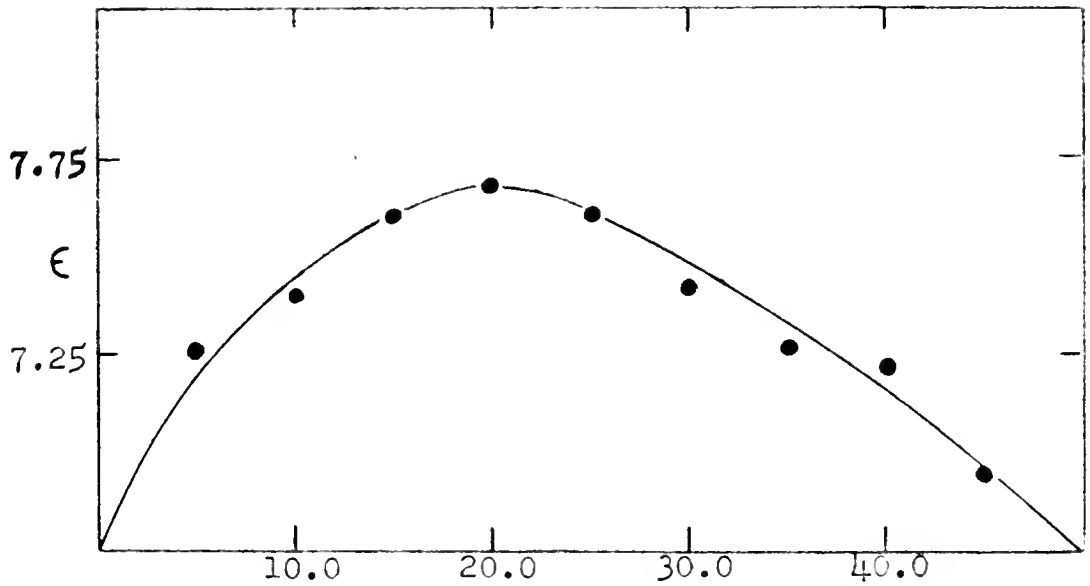


Fig. 11 - Di-isoamyl Sulfide-Dinitrogen Tetroxide

Measurements of Freezing Point Depression. The results of the measurements of freezing point depressions on the systems di-n-butyl sulfide-dinitrogen tetroxide and di-isoamyl sulfide-dinitrogen tetroxide are presented in Table 12.

The molal freezing point depression constant, K_f, was determined using a 0.029m N_2O_4-in-chloroform solution. A depression of 1.41° was noted for this solution, which, when substituted into the relation:

$$\Delta T = K_f \cdot m$$

gives a value for K_f of 48.6. Using this value and the measured freezing point depression, ΔT, for these solutions, the molality, m, of total species in solution was calculated. The solutions on which the measurements were made contained the sulfide and dinitrogen tetroxide in the mole ratio corresponding to the mole ratio at the maximum in their dielectric constant curves, viz., a ratio of sulfide to dinitrogen tetroxide of 2:3. With the assumption that the only species in these solutions are the addition compounds and uncombined sulfide and dinitrogen tetroxide molecules, the degree of dissociation, α, was calculated and is included in the results.

TABLE 12

FREEZING POINT DEPRESSION

System	ΔT	m	α
Di-n-butyl sulfide-dinitrogen tetroxide	1.47	0.030	0.58
Di-isoamyl sulfide-dinitrogen tetroxide	1.25	0.026	0.47

Oxidation of Dithiane with Dinitrogen Tetroxide. The reaction between 1,4-dithiane and dinitrogen tetroxide gave a solid product, which decomposed at 225-30°, and was found to contain sulfur and nitrogen. After recrystallization, the white solid decomposed at 263-5°, and was found to contain sulfur, but no nitrogen. This latter product was identified by its decomposition point and crystal structure (29) as mostly dithiane α-disulfoxide (trans form) and a small amount of dithiane β-disulfoxide (cis form).[4] Addition of dinitrogen tetroxide to some of the dithiane α-disulfoxide again gave the substance decomposing at 225-30°. This product is absolutely white at room temperature and has little or no odor. It is apparently an addition

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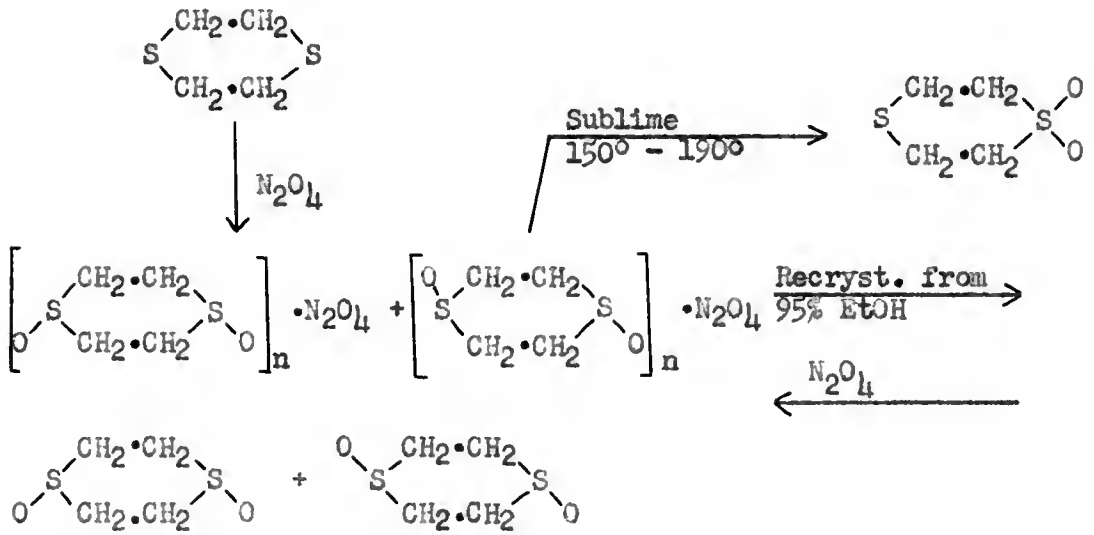
[4]Sincere appreciation is expressed to Miss Geraldine Westmoreland for her detailed study of the oxidation of dithiane by dinitrogen tetroxide in chloroform solution to give a mixture of the α- and β-disulfoxides of dithiane. Her study included a comparison between this method of preparation and the older method using hydrogen peroxide (29). It was her conclusion that the oxidation of dithiane to the disulfoxides of the dinitrogen tetroxide method is superior to that of the hydrogen peroxide method for the following reasons: (a) dinitrogen tetroxide produces only the disulfoxides in 100 per cent yield, whereas a slight excess of hydrogen peroxide is likely to cause further oxidation of the disulfoxides to the trioxide or disulfone; (b) the dinitrogen tetroxide method is less time consuming, requiring at most 12 hours, whereas the hydrogen peroxide method requires about two days; (c) the laboratory manipulations are simpler using dinitrogen tetroxide, since, if commercial dinitrogen tetroxide is used, the only laboratory operation beyond the very simplest is the removal of excess dinitrogen tetroxide with a water pump at the end of the experiment; use of hydrogen peroxide requires repeated steam distillations and evaporation of aqueous solutions to dryness.

Both methods produce predominately the α- or trans-disulfoxide and relatively little of the β- or cis-disulfoxide.

compound of dithiane ∝-disulfoxide and dinitrogen tetroxide, though a few quantitative determinations failed to show a definite mole ratio of sulfur to nitrogen. However, the ratio of sulfur to nitrogen was always high.

The white solid obtained from the sublimation of the dithiane ∝-disulfoxide-dinitrogen tetroxide addition compound contained sulfur, but no nitrogen. This compound was identified by its melting point of 205-7° to be dithiane monosulfone. The melting point of this compound has been reported variously in the literature as 200° (30), and 203° (31). Calculated for $C_4H_8S_2O_2$: C, 31.6 per cent; H, 5.2 per cent; found: C, 31.7 per cent; H, 5.4 per cent.[5]

These results may be summarized as follows:



[5]Analyses performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Mixing dinitrogen tetroxide with dithiane disulfone, under conditions similar to those for the reaction between dinitrogen tetroxide and dithiane α-disulfoxide, gave no reaction. The dithiane disulfone was recovered unchanged in 100 per cent yield.

DISCUSSION

Type of Addition Compound Formed Between the Sulfides and Dinitrogen Tetroxide. Addition compounds of dinitrogen tetroxide usually contain the dinitrogen tetroxide either in an essentially molecular form or in an essentially ionic form. We must consider which form is the more likely for the case of the sulfide-dinitrogen tetroxide addition compounds.

The donor atom in the sulfide Lewis bases is, of course, the sulfur atom. Since sulfur is a member of the oxygen family, it could perhaps be inferred that addition compounds of dinitrogen tetroxide involving sulfur as the donor atom should resemble addition compounds of dinitrogen tetroxide involving oxygen as the donor atom. From such an analogy, it would be concluded that the sulfide-dinitrogen tetroxide addition compounds contain dinitrogen tetroxide in the form of undissociated molecules. On the other hand, the sulfur atom is much larger than the oxygen atom. Mainly because of this size difference, the unshared electrons of sulfur are less strongly attracted by its nucleus than are the unshared electrons of oxygen. Consequently, sulfur should be a stronger electron donor than is oxygen. On this basis, it could be argued that the sulfides may be strong enough Lewis bases to lead to the dissociation of dinitrogen tetroxide into some

ionic species. It thus becomes evident that an attempt to predict the nature of the sulfide-dinitrogen tetroxide addition compounds by analogy with previously studied addition compounds of dinitrogen tetroxide is of little value.

Experimental evidence strongly suggests that the solid sulfide-dinitrogen tetroxide addition compounds are unstable under reduced pressure, even at low temperature. If the sulfides are strong enough Lewis bases to lead to the dissociation of dinitrogen tetroxide into ions, it would be reasonable to expect that the resulting addition compounds would, under reduced pressure, be stable with respect to dissociation into free acid and base. Thus, amines form addition compounds with dinitrogen tetroxide which are stable with respect to dissociation into free acid and base at quite low pressures, provided the temperature is low. Some of the heterocyclic amine-dinitrogen tetroxide addition compounds are thought to contain undissociated dinitrogen tetroxide in the solid state (12), dissociation occurring only in solution. It would seem unreasonable to think that the sulfide bases should be stronger electron donors than the heterocyclic amine bases and yet form addition compounds with dinitrogen tetroxide which show less stability under reduced pressure than the heterocyclic amine-dinitrogen tetroxide addition compounds. If, then, the sulfide bases are no stronger, and are probably even weaker, electron donors than the heterocyclic amine bases, it is reasonable to assume that in the solid state, the dinitrogen tetroxide in the sulfide-dinitrogen

tetroxide addition compounds is not dissociated into ions.

However, we must consider the possibility that even though the solid sulfide-dinitrogen tetroxide addition compounds contain molecular dinitrogen tetroxide, some dissociation into ions could occur in solution. The heterocyclic amine-dinitrogen tetroxide addition compounds are, as a rule, only sparingly soluble in ethyl ether. The sulfide-dinitrogen tetroxide addition compounds, however, are all soluble in ethyl ether, and, as a matter of fact, are apparently somewhat soluble in hexane. At least, they are very difficult to precipitate from this solvent. This evidence suggests that ionic species are not present to the significant extent in solutions of sulfide-dinitrogen tetroxide addition compounds.

One further possibility which must be considered is that in chloroform solutions, dissociation of the dinitrogen tetroxide into ions may occur. It is a fact that predominately ionic addition compounds of dinitrogen tetroxide with aliphatic amines show increased solubility in chloroform and other chlorinated hydrocarbons as compared with less polar solvents. It could be argued from this fact that perhaps chloroform is polar enough to cause the dissociation of dinitrogen tetroxide into some ionic species. From the data presented in Table 12, it can be seen that the freezing point depression is far less than that which would be expected on the assumption that either of these sulfides gives an addition compound with dinitrogen tetroxide in some ionic form. The formation of a 1:1 ionic type compound—the usual

stoichiometry for addition compounds where the dinitrogen tetroxide is ionic--should lead to a freezing point depression of about 2.2°, at the concentration employed, for both of the sulfide-dinitrogen tetroxide addition compounds. The degree of dissociation of an ionic type compound into free sulfide and molecular dinitrogen tetroxide should have no influence on the depression of the freezing point. The removal of a molecule of dinitrogen tetroxide and molecule of sulfide through the formation of an ionic type addition compound would lead to no reduction in total number of species present since a cation and an anion must be formed each time a molecule of dinitrogen tetroxide dissociates. The formation of addition compounds containing molecular dinitrogen tetroxide would, however, lead to a reduction in the total number of species present. There could, of course, be some equilibrium between a molecular type addition compound and an ionic type addition compound. As given in Table 12, the freezing point depressions of chloroform produced by the addition compounds of di-n-butyl sulfide and di-isoamyl sulfide with dinitrogen tetroxide are 1.47° and 1.25°, respectively. These depressions are fairly small for the concentration employed, and any such equilibrium could be expected to lie far to the side of the molecular type addition compound.

In summary, three types of evidence indicate that ionic species are absent, or at least unimportant, in the sulfide-dinitrogen tetroxide addition compounds. These are as follows: (a) the instability of the addition compounds under reduced pressure even at quite low

temperature with respect to dissociation into free acid and base; (b) the relatively high solubility of the addition compounds in solvents of low polarity; (c) the relatively small depression of the freezing point of chloroform caused by these addition compounds.

The possibility that nitrogen dioxide radicals may be involved in the addition compounds is remote. Certainly the equilibrium between dinitrogen tetroxide and nitrogen dioxide radicals in chloroform solutions at the temperatures at which the dielectric constant measurements were made would be displaced far to the dinitrogen tetroxide side. The dinitrogen tetroxide-chloroform solutions were absolutely colorless before mixing them with the sulfide-chloroform solutions. The phase diagram for the system chloroform-dinitrogen tetroxide (32) shows that no solid state compound exists between these substances, and the mole number calculated from the cryoscopic data is consistent with the dinitrogen tetroxide formulation. Studies of volume changes occurring on mixing dinitrogen tetroxide and chloroform, at 0° and below (33), show that the solutions are almost ideal. A very slight positive deviation from ideality is noted, but even this deviation decreases with decreasing temperature. It is recognized that the absence of nitrogen dioxide radicals before mixing the dinitrogen tetroxide-chloroform solutions and the sulfide-chloroform solutions does not absolutely preclude their formation and subsequent reaction after mixing the solutions. However, such a supposition lacks the slightest support from any of the previously studied addition compounds

of dinitrogen tetroxide and Lewis bases. Accordingly, the existence of nitrogen dioxide radicals in these addition compounds may be considered to be highly improbable.

The conclusion most consistent with the facts is that the sulfide-dinitrogen tetroxide addition compounds which were studied contain molecular dinitrogen tetroxide. It is upon this basis that the significance of the dielectric constant studies will be evaluated.

Dielectric Constant Studies. The capacitance, C, of a condenser is the ratio of the charge, Q, on one of its plates to the difference in potential, V, between its plates.

$$C = \frac{Q}{V}$$

The capacitance is a function of the physical dimensions of the particular condenser which is used as well as the nature of the dielectric, or insulation, between the condenser plates.[5]

The ratio of the capacitance of a condenser with some particular substance as the dielectric, C_D, to the capacitance of a condenser with no material dielectric, i.e., a vacuum between the plates, C_V, is the dielectric constant, ϵ .

$$\epsilon = \frac{C_D}{C_V}$$

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[5]Capacitance and, therefore, the dielectric constant are also functions of pressure and temperature. However, since these intensive variables are usually controlled, they do not represent additional degrees of freedom in a given experiment.

In practice, dry air is usually used instead of a vacuum, since in most work the difference in capacitance between dry air and a vacuum is negligible. If the same condenser, under identical conditions, is used to determine both C_D and C_V, the effects of the physical dimensions of the condenser on these quantities will cancel when the ratio is taken. It is thus unnecessary to know the condenser dimensions when measurements are made with the same instrument. The dielectric constant is independent of the particular condenser used and is a function only of the dielectric.[6]

The well-known Clausius-Mosotti equation relates the dielectric constant to the total molar polarization, P, of the dielectric.

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$$ where, M is molecular weight, d is density

This relation applies best to gases. When solutions are studied in which one of the components is a non-polar substance, the assumption is usually made that this relation still holds. If the mole fraction of component 1 be denoted as N_1 and the mole fraction of component 2 as N_2, then the Clausius-Mosotti equation assumes the form:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{N_1M_1 + N_2M_2}{d} = N_1P_1 + N_2P_2$$

If component 1 is taken to be the non-polar substance, then P_1 is its total molar polarization and is a constant throughout, and the quantity

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[6] Ibid.

N_1P_1 varies linearly with N_1. The quantity N_2P_2, and hence P_2, is then evaluated by difference. The changes of P_2 with N_2 are used to analyze the association process which occurs in such solutions (34).

There are several reasons why the chloroform solutions of the sulfide-dinitrogen tetroxide systems which were studied are not amenable to a treatment such as that just described. Chloroform is itself a somewhat polar substance. Yet, it was necessary to find a solvent which does not form a compound with dinitrogen tetroxide or with the sulfides, and at the same time, the solvent had to have a low enough freezing point to be a liquid at the low temperatures required to prevent oxidation-reduction. A consideration of these two factors strongly indicated use of chloroform as the solvent.

Even if a suitable non-polar solvent could have been found, an investigation over a large concentration range would have been impossible using the experimental technique previously described. Dinitrogen tetroxide is far too volatile to make even moderately concentrated solutions by the relatively simple direct weighing method used in this work. Even 0.1 molar solutions of dinitrogen tetroxide in chloroform (a very good solvent for dinitrogen tetroxide) are quite difficult to handle at room temperature without significant losses of dinitrogen tetroxide. To investigate a wide concentration range, more elaborate equipment would have been necessary. Should such equipment have been made, there would still have been an element of uncertainty in the interpretation of the results since three components

would have been involved—the solvent, dinitrogen tetroxide, and the sulfide. Since one of the purposes of this study was to try to determine the stoichiometry of the sulfide-dinitrogen tetroxide addition compounds, the necessary information to reduce the three variables to two variables—solvent and addition compound—would have been lacking. Whether one would have been studying the association of the sulfides with dinitrogen tetroxide, or the association among the resulting addition compounds themselves, would not have been clear. Undoubtedly, both of these effects would have manifested themselves in the dielectric constant measurements. The separation of these effects would pose a formidable, if not impossible, theoretical problem.

The fact that chloroform is somewhat polar has an advantage, however. Its polarity gives rise to a dielectric constant, at the temperatures employed, high enough to mask completely the contributions of the dinitrogen tetroxide and the sulfides in the separate chloroform solutions. It is felt that the increase in dielectric constant above that of the separate solutions (essentially pure chloroform) is therefore attributable almost completely to the resulting addition compound. The maximum concentration used was 0.065 molar for the separate solutions of the sulfides and of dinitrogen tetroxide. The formation of an addition compound can only lead to a final concentration of the addition compound which is less than the original concentration of the separate solutions. It is reasonable to conclude that the concentrations of all the addition compounds studied were small

enough to preclude significant interaction among the addition compound molecules themselves.

Some interaction must occur between chloroform and the addition compounds. To deny such an interaction would be completely unjustified. Yet, it seems altogether justifiable to assume that such solvation of the addition compounds by the chloroform is of a similar nature for all of the compounds since the studies involved an essentially homologous series of sulfides reacting with dinitrogen tetroxide. If we proceed upon such an assumption, then, even though a quantitative argument is of doubtful value, qualitative and semi-quantitative trends shown by the dielectric constants of the various sulfide-dinitrogen tetroxide systems can be interpreted in terms of trends to be found among the addition compounds alone.

At the relatively low frequency used for the dielectric constant measurements, the total molar polarization of any species is composed mainly of two factors. First, there is the contribution from the presence of any permanent electric moment or permanent dipole moment. Second, there is the contribution from transitory or induced dipoles which arise from the imposed electric field, and which also may possibly arise from an electric field created by the nearby presence of another molecule possessing a permanent or an induced dipole. All molecules exhibit this second type of polarization to some degree. Only in those molecules where there exists a permanent asymmetry of charge distribution is the first type of polarization,

that caused by a permanent moment, exhibited.[7]

The magnitude of the permanent polarization is dependent upon the temperature. The higher the temperature the greater the thermal agitations of the polar species. This thermal agitation prevents an efficient alignment of the dipole in the imposed electric field, thus lowering the measured polarization. Induced polarization does not show this temperature dependence.

Induced polarization is composed primarily of electronic asymmetry produced by the imposed electric field or by the presence of a field established by a neighboring species. The atoms of a molecule may also have their nuclei slightly displaced by an imposed electric field and hence contribute to the induced polarization. However, since electrons are relatively mobile compared to the nuclei of atoms, by far the more important factor of induced polarization is the electronic effect. It will be assumed that electronic polarization is the only induced polarization effect that need be considered in the discussion of the sulfide-dinitrogen tetroxide addition compounds.

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[7]A definite time, the relaxation time, is required for permanent dipoles to revert to a random distribution after the removal of the impressed field. If the frequency of the alternating field is of the same order of magnitude as the relaxation time, the dipole cannot re-orient itself, and only induced polarization is measured. Since the relaxation time for a wide variety of polar molecules is of the order of 10^{-11} seconds, this effect does not appear until the frequency of the field approaches 10^{10} cycles/second and almost certainly is not present when the frequency is less than 10^{8} cycles/second.

We may write:

$P = P_u + P_E$ where, P_u is the permanent polarization
P_E is the induced (electronic) polarization

and, as before:

$$P_u + P_E = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$$

Since the assumption of non-interaction between chloroform and the addition compounds cannot be made, there is no way to obtain a simple relation for $P_u + P_E$ which would apply to the addition compounds alone. However, if the assumption, previously discussed, that trends in the total polarization may be largely ascribed to changes in the addition compounds alone is valid, then we may say:

$$(P_u + P_E)_{\substack{\text{addn.} \\ \text{comp.}}} \propto \frac{(\epsilon - 1)}{(\epsilon + 2)}$$

In Table 13, are listed values (multiplied by 10^3 for convenience) of the quantity, $\frac{(\epsilon - 1)}{(\epsilon + 2)}$ for the maximum dielectric constant measured for the sulfide-dinitrogen tetroxide systems. Also listed are the relative changes in this quantity (and hence in the quantity $P_u + P_E$) in moving from addition compound to addition compound in the essentially homologous sulfide series.

Basically, three points must be considered in discussing the sulfide-dinitrogen tetroxide addition compounds and their electrical behavior. These points are the following: (a) the trends

TABLE 13

RELATIVE POLARIZATIONS OF THE SULFIDE - DINITROGEN TETROXIDE ADDITION COMPOUNDS AT -60°

System	$\left[\frac{(\epsilon - 1)}{(\epsilon + 2)}\right] \times 10^3$ max.	$(P_u + P_E) \times 10^3$
Dimethyl sulfide-dinitrogen tetroxide	676	-
Diethyl sulfide-dinitrogen tetroxide	683	+7
Di-n-propyl sulfide-dinitrogen tetroxide	693	+10
Di-n-butyl sulfide-dinitrogen tetroxide	692	-1
Di-isoamyl sulfide-dinitrogen tetroxide	690	-2

presented in Table 13; (b) the reasons why not all the sulfide-dinitrogen tetroxide addition compounds studied show a significant increase in dielectric constant, and hence in polarization, over and above that of chloroform, and the reason why none of the three analogous ether-dinitrogen tetroxide systems studied produces much change from the dielectric constant of chloroform alone; (c) the significance of the stoichiometries indicated by the maxima of figures 7 through 11. These three points will be considered in order, as listed. Electric moment data, relative to the future discussion, for some ethers and sulfides are presented in Table 14

(35), (36), (37). Included in these data are permanent dipole moments in Debye units for the ethers and sulfides, and the induced electronic polarization in cubic centimeters for the sulfides.

TABLE 14

ELECTRIC MOMENT DATA FOR SOME SULFIDES AND ETHERS

Substance	u (Debye units)	P_E (c.c.)
Hydrogen sulfide	1.10	-
Dimethyl sulfide	1.40	19.1
Diethyl sulfide	1.57	28.46
Di-n-propyl sulfide	1.55	37.6
Di-n-butyl sulfide	1.57	46.9
Water	1.87	-
Methyl ether	1.29-1.32	-
Ethyl ether	1.10-1.14	-
n-Propyl ether	1.16	-

It has been recognized for some time that the replacement of a hydrogen atom by a methyl group in a molecule has two chief effects on a functional group in the molecule (38). The permanent polarization and the polarizability of the molecule in question are likely to be affected. Table 14 shows that as methyl groups successively replace hydrogen atoms in the sulfides, there is a sharp increase in the

permanent dipole moment until diethyl sulfide is reached, after which, further substitution of methyl groups has no significant effect. The usual explanation for this behavior is that the greater polarizability of methyl groups over hydrogen atoms allows the sulfur atom to draw electrons to itself more efficiently. This effect is one of a permanent induction along the hydrocarbon chain, which results in a greater degree of permanent polarization within the molecule. However, this effect dies out as soon as there is more than one saturated carbon atom between the sulfur atom and the additional methyl group. This phenomenon is referred to as the "insulation effect" of saturated carbon atoms. This effect explains why the permanent dipole moment remains constant when diethyl sulfide is reached. In addition to increasing the permanent polarization of the molecule, the substitution of methyl groups for hydrogen atoms also causes the functional group to display greater polarizability. When the sulfides act as Lewis bases, there must be present, of course, some Lewis acid—in this case, dinitrogen tetroxide. An increase in the permanent polarization of the sulfide would increase its strength as a Lewis base toward dinitrogen tetroxide, by making the electrons more available to the dinitrogen tetroxide. However, an increase in the polarizability of the sulfide would also increase its strength as a Lewis base by making it easier for the dinitrogen tetroxide to attract to itself the unshared electrons on the sulfur atom. This greater polarizability does not manifest itself until the sulfur atom is under attack by the dinitrogen tetroxide.

Naturally, the polarization and polarizability effects which were discussed in the preceding paragraph would operate whenever a sulfide-dinitrogen tetroxide addition compound is formed, regardless of whether one happened to be measuring the dielectric constant of the compound or not. However, that the presence of a methyl group in place of a hydrogen atom does lead to a greater polarizability is reflected in the P_E term. The imposed electric field distorts the molecules still more as methyl groups are substituted for hydrogen atoms. Table 14, indeed, shows that the P_E term continues to increase regularly as methyl groups are substituted in the molecules.

It is now possible to suggest an explanation for the trend in Table 13. The increase in polarization of the diethyl sulfide-dinitrogen tetroxide addition compound as compared with the dimethyl sulfide-dinitrogen tetroxide addition compound reflects the increased permanent moment of diethyl sulfide over dimethyl sulfide. The greater dipole moment of diethyl sulfide probably leads to a greater separation of charge, or permanent dipole moment, in the diethyl sulfide-dinitrogen tetroxide addition compound. Furthermore, the greater polarizability of diethyl sulfide may allow dinitrogen tetroxide to cause greater distortion of the sulfur atom in diethyl sulfide than in dimethyl sulfide. Such an increased distortion of the sulfur atom should also help to increase the permanent dipole moment of the diethyl sulfide-dinitrogen tetroxide addition compound.

The increased distortion of the sulfur atom by dinitrogen

tetroxide in the diethyl sulfide addition compound as compared with the dimethyl sulfide addition compound may also lead to a greater induced polarization by the imposed electric field. At first, it may seem unreasonable to suggest that increased displacement of the elctrons on the sulfur atom may make it easier to displace electrons even more by application of an external field. But it must be remembered that this discussion does not involve molecules of diethyl or dimethyl sulfides alone, but rather these molecules as they exist in an addition compound with dinitrogen tetroxide. Attention can no longer be centered on the sulfur atoms alone. It is simply being suggested that when, by substitution of a methyl group for a hydrogen atom, the sulfur atom is more easily polarized by dinitrogen tetroxide, the electronic distribution of the resulting compound may be more susceptible to displacement by an external field. For example, the more completely the nitrogen atoms in a molecule of dinitrogen tetroxide gain control of electrons from the sulfur atoms, the more completely the oxygen atoms gain control of the electrons constituting the bond between the nitrogen and oxygen atoms. The creation of the additional formal charges on the oxygen atoms could lead to greater induced polarization.

The relatively large increase in polarization, noted in Table 13, of the di-n-propyl sulfide-dinitrogen tetroxide addition compound over the diethyl sulfide-dinitrogen tetroxide addition compound probably is a result of increased polarizability of the sulfur atom. The permanent dipole moment of di-n-propyl sulfide is about the same as

that of diethyl sulfide because of the insulation effect. The greater polarizability of the sulfur atom in di-n-propyl sulfide would allow greater distortion by dinitrogen tetroxide and hence a greater permanent dipole moment in the di-n-propyl sulfide addition compound as compared with the diethyl sulfide addition compound. Also, a greater distortion may produce a greater subsequent induced polarization, as previously suggested.

The two remaining addition compounds in Table 13 not only show no further increases in total polarization but even exhibit slight decreases from the di-n-propyl sulfide-dinitrogen tetroxide addition compound. One reason for this observation may be a steric effect coming into play as the hydrocarbon chain lengthens in the successive sulfide molecules. The relatively large n-butyl and isoamyl groups could serve to decrease the total polarization of the addition compounds in which they are present by limiting the number of molecules of dinitrogen tetroxide in the addition compounds or possibly by assuming such positions as to cause a slight cancellation of permanent or induced polarizations, or perhaps both, in their addition compounds.

It has now been suggested that three factors may cause the trend to be found in Table 13. First, an increase in the permanent dipole moment of the sulfide molecule leads to a greater permanent dipole moment, and hence to a greater total polarization in the resulting addition compound. Second, the polarizability of the sulfide

molecule increases as methyl groups are substituted for hydrogen atoms. This greater polarizability may help to increase the permanent polarization of the addition compound and it may also help to increase the induced polarization of the addition compound. Third, steric effects may become an important factor as the hydrocarbon chains in the sulfides lengthen. The first factor probably helps to increase the total polarization of the diethyl sulfide-dinitrogen tetroxide addition compound over that of the dimethyl sulfide-dinitrogen tetroxide addition compound. This factor probably does not lead to further increases in the total polarization of the sulfide-dinitrogen tetroxide addition compounds involving sulfide homologs higher than diethyl sulfide. The second factor probably contributes to an increase in total polarization for each successive addition compound in the series. The third factor probably becomes important in the di-n-butyl sulfide-dinitrogen tetroxide addition compound. This factor would oppose the second factor and tend to decrease the total polarization of the addition compounds of higher sulfide homologs.

A few dielectric constant measurements at temperatures higher than -60° (Tables 2 and 6) show a general decrease in polarization with increasing temperature for the addition compounds. This fact indicates the presence of a permanent dipole moment in these addition compounds.

Bis-(chloromethyl) sulfide and dinitrogen tetroxide apparently do not form an addition compound under conditions similar to those

employed with the other sulfides and dinitrogen tetroxide. The absence of any color when the two are mixed and the lack of an increase in the dielectric constant over that of chloroform alone suggest that no compound is formed. Color is apparently a good indication of the formation of an addition compound between an organic sulfide and dinitrogen tetroxide. There is fairly good correlation between total polarization and color. To some extent, the higher is the total polarization of the addition compounds, the deeper red are their colors. This effect is quite noticable among the addition compounds where large changes in polarization occur. However, the colors of both the di-n-butyl and the di-isoamyl sulfide-dinitrogen tetroxide compounds are very deep red; in fact, they are a bit deeper red than the di-n-propyl sulfide-dinitrogen tetroxide addition compound. The differences in color, as well as the differences in polarization are, however, fairly small for these three addition compounds. Shifts to longer wave lengths in the colors of compounds are usually connected with a general lowering of the energy of the system. The lack of any color when an organic sulfide is mixed with dinitrogen tetroxide, at low temperatures, can be ascribed to the lack of any lowering in energy of the system, and thus to a lack of any strong interaction between the molecules. The reason that bis-(chloromethyl) sulfide does not form an addition compound with dinitrogen tetroxide, under the same conditions as those for the other sulfide-dinitrogen tetroxide systems, is probably because the rather electronegative chlorine atoms

decrease the electron density on the sulfur atom to such an extent that electron donation by sulfur to dinitrogen tetroxide is not possible.

Reference to Table 14 shows that the ethers do not follow the same trend as do the sulfides with respect to their permanent dipole moments. The permanent dipole moments of the ethers do not increase as methyl groups are substituted for hydrogen atoms; rather, just the opposite effect is observed. Oxygen is not nearly as polarizable an atom as sulfur. This fact plus the fact that the relatively small size of the oxygen atom gives rise to a shielding or steric interference by hydrocarbon chains (39) probably are primarily responsible for this difference between the sulfides and the ethers. This reasoning also explains why addition compounds between ethers and dinitrogen tetroxide should show less polarization than the corresponding sulfide-dinitrogen tetroxide addition compounds. The systems n-butyl ether-dinitrogen tetroxide and 1,4-dioxane-dinitrogen tetroxide in chloroform solutions (Tables 9 and 11, respectively) show an almost negligible change in dielectric constant from that of chloroform. The more basic tetrahydropyran shows a very slight increase in dielectric constant over chloroform when mixed with dinitrogen tetroxide in the usual manner (Table 10). These very slight changes in dielectric constant seem to indicate that interaction is occurring, but that the total polarization of the resulting compounds adds only slightly to the already moderately high polarization of chloroform alone. If the relatively stable cyclic structure of the 1,4-dioxane-dinitrogen tetroxide addition

compound is retained in chloroform solutions, this structure could perhaps lead to a partial cancellation of charge separation and help to reduce the total polarization.

The data for the system 1,4-dithiane-dinitrogen tetroxide (Table 8) show a slight drift to higher dielectric constants as the ratio of dinitrogen tetroxide to dithiane becomes very high. The pale color which does appear, does so only after an induction period following the mixing of the solutions. One possible explanation is that when the stoichiometry is anywhere near equi-molar amounts of dithiane and dinitrogen tetroxide, the structure of the addition compound resembles that of the cyclic structure of the dioxane-dinitrogen tetroxide addition compound. Calculations show that the dioxane molecule in the "boat" form is sterically favorable for the formation of a cyclic structure (2). In view of the much larger size of the sulfur atom as compared with the oxygen atom, it is probable that an analogous dithiane-dinitrogen tetroxide addition compound would not be nearly as stable as the dioxane addition compound. Interference between the sulfur atoms in the "boat" form of dithiane would be much more severe than interference between oxygen atoms in the "boat" form of dioxane. The "chair" configuration for dithiane is thermodynamically favored, as would be expected (40), (41). It is likely that the conversion from the "chair" to the "boat" configuration would require a significantly higher activation energy in the case of dithiane than for dioxane. The induction period before the appearance of a color

after mixing the dithiane and dinitrogen tetroxide solutions can be explained as the time required for "chair" dithiane to convert to "boat" dithiane and then collide with a dinitrogen tetroxide molecule in precisely the right way to form the relatively unstable cyclic structure. Increasing the ratio of dinitrogen tetroxide to dithiane may lead to the interaction of more molecules of dinitrogen tetroxide with the dithiane which has already formed the cyclic addition compound with dinitrogen tetroxide. Since both ends of the same dithiane molecule would be under attack by dinitrogen tetroxide molecules, further steric hindrance would be likely. The net effect of the unfavorable spatial arrangements would be less efficient electron donation and acceptance and, consequently, a relatively low total polarization.

Reference to the curves in figures 7 through 11 shows a change in the position of the maximum of the dielectric constant curves for the addition compounds as the sulfides are changed. Table 15 gives the ratio of sulfide to dinitrogen tetroxide at the maximum dielectric constant for these systems as read from the graphs.

The weakest base, dimethyl sulfide, forms a 1:1 addition compound with dinitrogen tetroxide in chloroform solution. There is a sharp change in the apparent stoichiometry for the diethyl sulfide-dinitrogen tetroxide addition compound; the proportion of dinitrogen tetroxide is much higher in the latter compound. After diethyl sulfide, the remaining sulfide-dinitrogen tetroxide addition compounds show a

TABLE 15

APPARENT STOICHIOMETRY OF THE SULFIDE - DINITROGEN TETROXIDE COMPOUNDS IN CHLOROFORM SOLUTION FROM DIELECTRIC CONSTANT MEASUREMENTS

System	Mole Ratio: R_2S/N_2O_4 at $\epsilon_{max.}$
Dimethyl sulfide-dinitrogen tetroxide	1:1
Diethyl sulfide-dinitrogen tetroxide	1:2.5, or 2:5
Di-n-propyl sulfide-dinitrogen tetroxide	1:2
Di-n-butyl sulfide-dinitrogen tetroxide	1:1.5, or 2:3
Di-isoamyl sulfide-dinitrogen tetroxide	1:1.5, or 2:3

gradual reduction in the proportion of dinitrogen tetroxide. These apparent empirical formulas for the addition compounds apply to the compounds dissolved in chloroform. From the experimental data obtained in this work, it is impossible to assess accurately the effect of the solvent upon the apparent empirical formulas. Furthermore, empirical formulas for the solid addition compounds could not be obtained. Therefore, the discussion of the significance of these results in solution cannot be assumed to apply necessarily to the solid-state addition compounds.

The 1:1 stoichiometry observed for the dimethyl sulfide-dinitrogen tetroxide compound is not at all surprising. The large size of sulfur may sterically prohibit electron donation by two sulfide molecules to a single dinitrogen tetroxide molecule even from opposite ends of the dinitrogen tetroxide molecule. The fairly strong basicity of the sulfide may allow partial donation of electrons to both nitrogen atoms in dinitrogen tetroxide from the same sulfur atom. Some of the more basic monofunctional ethers form 1:1 addition compounds with dinitrogen tetroxide, as well as the $N_2O_4 \cdot 2B$ type of compound.

The change to the relatively high ratio of dinitrogen tetroxide to sulfide in the diethyl sulfide addition compound is probably a reflection of the large degree of polarization of diethyl sulfide as compared with dimethyl sulfide. Since electrons are more readily available to dinitrogen tetroxide from diethyl sulfide, than from dimethyl sulfide, a more favorable electronic distribution may occur

when more than one molecule of dinitrogen tetroxide takes part in the electron sharing process. The large sulfur atom is probably not sterically hindered to a great extent by the ethyl groups.

Di-n-propyl sulfide is more basic than diethyl sulfide, but the propyl groups may exert enough steric hindrance to begin to limit the number of dinitrogen tetroxide molecules which can efficiently group themselves around the sulfur atom. As previously suggested, the steric factor may become important with di-n-butyl sulfide and di-isoamyl sulfide. This factor could explain the further decrease of moles of dinitrogen tetroxide per mole of sulfide for these addition compounds. As has already been pointed out, electronic effects tend to lead to increased polarization of the addition compounds as the hydrocarbon chain of the sulfide lengthens. However, steric hindrance also increases as the hydrocarbon chain lengthens and may tend to decrease the total polarization. Apparently the most favorable balance between these opposing factors, as far as total polarization is concerned, is found in the di-n-propyl sulfide-dinitrogen tetroxide addition compound, as exemplified by the magnitude of the $\epsilon_{max.}$ values. Permanent polarization and polarizability effects are high in this addition compound and steric effects, though beginning to appear, do not seriously interfere. As a result, the di-n-propyl sulfide-dinitrogen tetroxide addition compound shows the largest total polarization.

The $R_2S:N_2O_4$ mole ratio of 1:2.5 for the diethyl sulfide-dinitrogen tetroxide addition compound can, of course, be written

2:5, suggesting that perhaps more than one sulfide molecule is to be found in a molecule of the addition compound. This argument is based upon the assumption that only one complex is formed in the system and that there is no complication, as was mentioned on page 15 of this dissertation, arising from the presence of more than one equilibrium in the system. These same possibilities also apply to the di-n-propyl sulfide and di-isoamyl sulfide addition compounds, which also show fractional mole ratios. The experimental technique employed may simply be too insensitive to detect the true mole ratios. Even if this should be the case, it is felt that the general discussion which has been presented would be applicable.

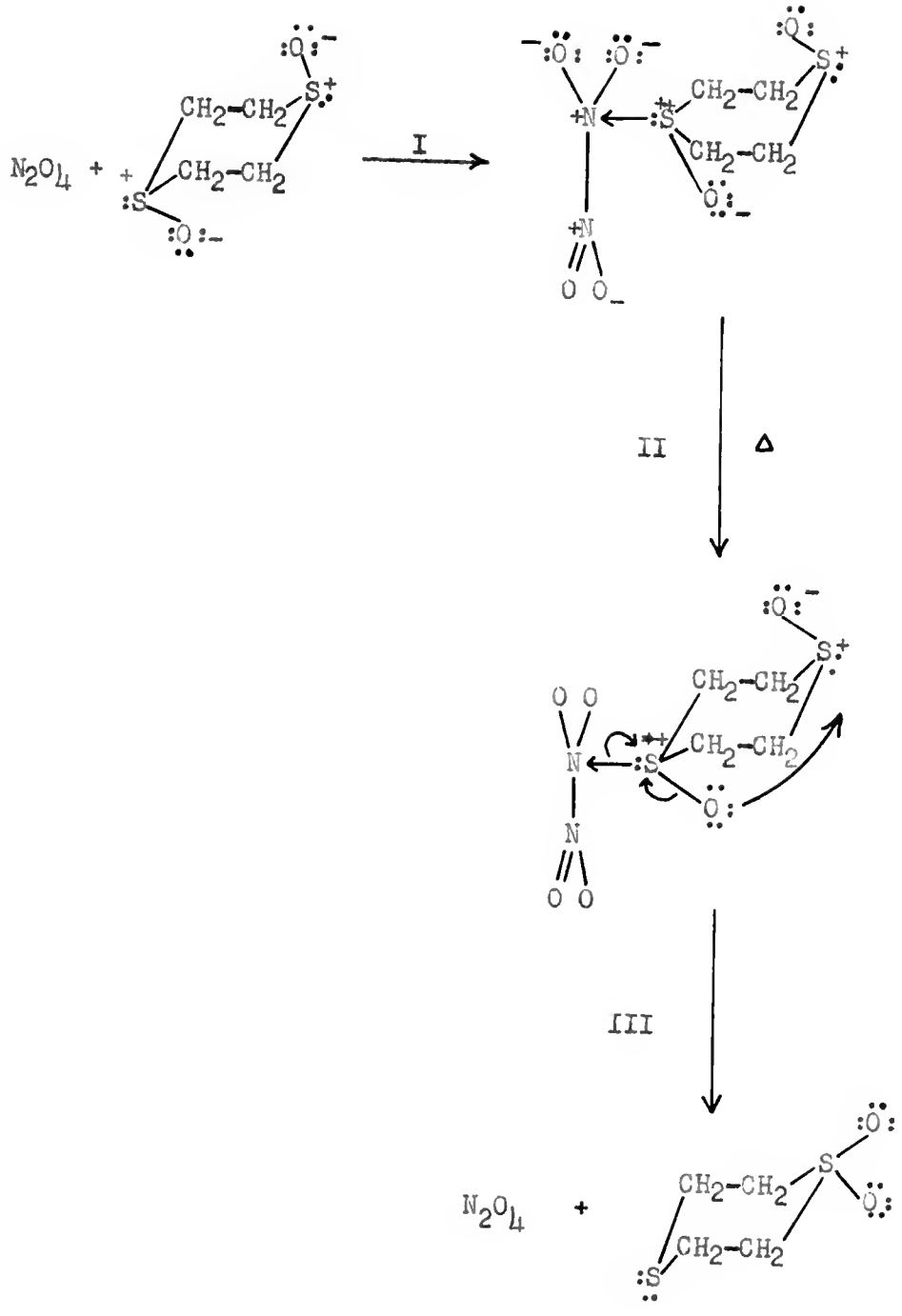
Finally, we should consider the shape of the curves in figures 7 through 11. There is a sharpening of the maximum as we pass successively from the dimethyl sulfide-dinitrogen tetroxide system to the di-isoamyl sulfide-dinitrogen tetroxide system. The simplest explanation for this behavior is analogous to that employed to explain variation of sharpness of maxima in temperature-concentration phase diagrams; viz., that "flatness" indicates dissociation of the compound into its component parts. The sharper the maximum, the less is the dissociation. In order to test this idea, a calculation, based on cryoscopic measurements, of the degree of dissociation, of the two addition compounds showing the same stoichiometry at the maximum in their dielectric constant curves was made (Table 12). Di-n-butyl

sulfide and di-isoamyl sulfide show the same stoichiometry with dinitrogen tetroxide (Table 15). However, the di-n-butyl sulfide-dinitrogen tetroxide system, according to the calculation, shows a higher degree of dissociation than the di-isoamyl sulfide-dinitrogen tetroxide system. Likewise, the dielectric constant curve for the di-n-butyl sulfide-dinitrogen tetroxide system (Fig. 10) is not quite as sharp at its maximum as is the curve for the di-isoamyl sulfide-dinitrogen tetroxide system (Fig. 11). Though this one comparison does not prove this reasoning conclusively, it at least presents evidence from a different experimental source which is consistent with the interpretation which has been suggested for the shapes of the dielectric constant curves.

If total polarization is assumed to parallel thermodynamic stability, we are unable to explain why the di-n-butyl sulfide and di-isoamyl sulfide addition compounds should apparently show less dissociation according to the criterion of the shapes of the curves while, at the same time, the di-n-propyl sulfide addition compound should show the highest total polarization of the compounds studied. The answer may simply be that although large changes in total polarization give an indication of relative stabilities, total polarization may, nevertheless, not be a strict index of the thermodynamic stability of the addition compounds. It has been pointed out that steric factors may be responsible for decreasing slightly the total polarization of the higher sulfide homolog addition compounds from the total polarization of the di-n-propyl sulfide addition compound. But this small

decrease in polarization does not necessarily reflect any decrease in thermodynamic stability. The generally deeper red colors of the addition compounds and the generally sharper maxima of their dielectric constant curves as one proceeds up the homologous series of sulfides actually indicates that thermodynamic stability increases throughout.

Oxidation of Dithiane with Dinitrogen Tetroxide. The only puzzling aspect of the series of reactions associated with the oxidation of 1,4-dithiane by dinitrogen tetroxide is the formation of 1,4-dithiane monosulfone as a sublimation product of the 1,4-dithiane α-disulfoxide-dinitrogen tetroxide addition compound. The oxidation of dithiane by dinitrogen tetroxide to give mostly dithiane α-disulfoxide plus a little dithiane β-disulfoxide was to be expected by analogy with the oxidation of the aliphatic sulfides. The formation of some addition compound between dinitrogen tetroxide and the disulfoxides was also to be expected by analogy with the aliphatic sulfoxides. The reversibility of the reaction of dithiane α-disulfoxide with dinitrogen tetroxide proves that there is no rearrangement within the molecules when the reaction is carried out at room temperature or below. Strong heating does lead to rearrangement, however, and the following mechanism for the formation of dithiane monosulfone is offered in an attempt to explain this fact.


I
II
Δ
III

Step I is the formation of some addition compound between dithiane ∝-disulfoxide and dinitrogen tetroxide. The formation of such an addition compound would give rise to a formal charge distribution as indicated. A nitrogen to sulfur linkage, rather than a nitrogen to oxygen linkage, is indicated for the addition compound since neither the alkyl sulfone nor dithiane disulfone form addition compounds with dinitrogen tetroxide. Dithiane ∝-disulfoxide is known to have the "chair" configuration as pictured (42). The sulfoxide oxygen atoms are approximately 3.5Å from the other sulfur atom to which they are not bonded. This distance is somewhat over twice the normal sulfur-oxygen bond distance, but it is close enough for van der Waals forces to operate. The presence of the dinitrogen tetroxide in the addition compound could further reduce this distance, as indicated. The high formal charge on the sulfur atom which is donating electrons to the nitrogen would offer the possibility of the electronic rearrangement at high temperatures as pictured in Step II. If such a rearrangement occurred, the lower oxygen atom would become positive and would migrate toward the pair of electrons on the sulfur atom to which it was not originally bonded. The final products are given by Step III.

Of course, the second oxygen atom which is added to one of the sulfur atoms to give the sulfone may come from the dinitrogen tetroxide molecule, but if so, the abstraction of oxygen from the other sulfur atom remains to be explained. The suggested mechanism accounts for all the observed facts.

Oxidation of Trithiane with Dinitrogen Tetroxide. Dinitrogen tetroxide does not oxidize trithiane smoothly, as it does dithiane. Apparently ring cleavage occurs with trithiane. Other Lewis acids are known to cause ring cleavage with trithiane. Aluminum chloride in benzene (43) and chlorine water (44) both lead to the production of free sulfur, among other things, when reacted with trithiane.

The amorphous nature of the residue from the reaction of dinitrogen tetroxide with trithiane and its low solubility in a variety of solvents suggest the formation of polymeric substances. Polymeric ethylene sulfides are known (45), and it is not unlikely that products of a similar nature are formed in this reaction.

SUMMARY

At temperatures near -60°, aliphatic and alicyclic sulfides react with dinitrogen tetroxide to form Lewis acid-base type addition compounds. Previous work had shown that at higher temperatures, oxidation-reduction occurs, leading to the formation of the corresponding sulfoxides for the aliphatic sulfides. The present work has shown that a similar oxidation-reduction occurs with 1,4-dithiane, but that ring cleavage occurs with trithiane to produce free sulfur, volatile sulfur containing substances, and polymeric materials.

Evidence has been presented to show that the aliphatic sulfide-dinitrogen tetroxide addition compounds contain molecular dinitrogen tetroxide. In this respect, they resemble the ether-dinitrogen tetroxide addition compounds. Measurements of the dielectric constants of these sulfide-dinitrogen tetroxide addition compounds and also of some of the ether-dinitrogen tetroxide systems, both in chloroform solutions, indicate that the sulfide-containing addition compounds are much more polar than analogous ether containing addition compounds. This fact can be attributed to the larger dipole moments of the sulfides compared with the ethers and the greater polarizability of the sulfur atom than of the oxygen atom. Both of these effects can lead to a greater total polarization of the sulfide-dinitrogen tetroxide addition

compounds than of the ether-dinitrogen tetroxide addition compounds.

The relative total polarizations of the sulfide-dinitrogen tetroxide addition compounds in chloroform solutions are found to increase, at first, as methyl groups are substituted for hydrogen atoms in the hydrocarbon chains of the sulfide molecules. A maximum in total polarization is reached with the addition compound containing di-n-propyl sulfide. Further substitution of methyl groups in the sulfide molecules gives addition compounds with dinitrogen tetroxide which show slight decreases in total polarization from the di-n-propyl sulfide-dinitrogen tetroxide addition compound. Three factors are suggested as the cause of this trend. These factors are: (a) the increase in the permanent dipole moment of the sulfides, as methyl groups are substituted for hydrogen atoms until diethyl sulfide is reached, leads to greater Lewis base strength in the sulfides and, consequently, to a greater permanent dipole moment in the resulting addition compound; (b) the increase in the polarizability of the sulfides, as methyl groups are substituted for hydrogen atoms, can lead to a greater permanent dipole moment and a greater induced moment in the resulting addition compound; (c) the greater possibility for steric hindrance from the hydrocarbon chains of the sulfides, as methyl groups are substituted for hydrogen atoms, may lead to a reduction in the permanent or induced moments, or perhaps both, in the resulting addition compound.

Increases in thermodynamic stability of the sulfide-dinitrogen tetroxide addition compounds apparently accompany large increases in

the total polarization of the compounds. Small changes in total polarization of these addition compounds are, however, not necessarily connected with their stability. There are indications that the stability of the addition compounds increases continuously as higher homologs of the sulfides are used, up through di-isoamyl sulfide.

The dielectric constant data were treated so that an analysis using Job's method of continuous variations is possible. In chloroform solutions, the addition compound between dimethyl sulfide and dinitrogen tetroxide shows a 1:1 stoichiometry. The diethyl sulfide addition compound shows a much higher ratio of dinitrogen tetroxide than the dimethyl sulfide addition compound. A ratio of 1:2.5 (or 2:5) for diethyl sulfide to dinitrogen tetroxide is found for this addition compound. The ratio is 1:2 for di-n-propyl sulfide to dinitrogen tetroxide, and 1:1.5 (or 2:3) for both di-n-butyl sulfide and di-isoamyl sulfide to dinitrogen tetroxide. The large increase in the proportion of dinitrogen tetroxide to sulfide for the addition compound involving diethyl sulfide as compared with the addition compound involving dimethyl sulfide is interpreted as a reflection of the increase in basicity of diethyl sulfide as compared with dimethyl sulfide. The gradual decrease in the proportion of dinitrogen tetroxide to sulfide in the remaining addition compounds is interpreted as reflecting an increase in steric hindrance as the hydrocarbon chain of the sulfide lengthens.

The lack of formation of a stable addition compound in

chloroform solutions of 1,4-dithiane and dinitrogen tetroxide is attributed to unfavorable steric effects. The possibility of partial cancellation of separation of charges, and consequent decrease in polarization, due to the formation of a cyclic structure, is also considered. The lack of formation of an addition compound in chloroform solutions of bis-(chloromethyl) sulfide and dinitrogen tetroxide is attributed to a decrease in basicity of the sulfide resulting from the presence of the relatively electronegative chlorine atoms.

Dinitrogen tetroxide and 1,4-dithiane α-disulfoxide form a solid, white addition compound, which is stable at room temperature. Consistent mole ratios of the disulfoxide to dinitrogen tetroxide in this addition compound were not obtained. However, the ratio of disulfoxide molecules to dinitrogen tetroxide is fairly high in the compound. Sublimation of this addition compound at temperatures above 150° leads to the formation of dithiane monosulfone. A mechanism is suggested for this rather unexpected reaction.

APPENDIXES

APPENDIX I

JOB'S METHOD OF CONTINUOUS VARIATIONS

Assume the following equilibrium:

$$A + nB \rightleftharpoons AB_n$$

Suppose that solutions of A and B are prepared, both with a concentration of M moles per liter, and that they are mixed in varying proportions while always keeping the total volume, V, fixed. Assuming volumes are additive, this procedure will maintain a constant initial total number of moles of A and B.

For convenience, the following notation will be used for the system at equilibrium:

$$[A] = C_1$$

$$[B] = C_2$$

$$[AB_n] = C_3$$

The following relations hold at equilibrium:

(1) $C_1 = \frac{M(V - x)}{V} - C_3$ where, x = volume of solution B taken

(2) $C_2 = \frac{Mx}{V} - nC_3$

(3) $K_{eq} = \frac{C_3}{C_1 C_2^n}$ assuming that the equilibrium constant may be expressed in terms of concentrations.

If C_3 is expressed as a function of $\underline{x}$, by the measurement of a suitable physical property as $\underline{x}$ is varied, the necessary condition for a maximum or a minimum in the function is:

(4) $C_3' = 0$ where, C_3' is the first derivative of C_3 with respect to $\underline{x}$.

From (3):

(3') $C_3 = K_{eq} C_1 C_2^{\,n}$

Differentiation of (1), (2), and (3') with respect to $\underline{x}$ gives:

(1') $C_1' = \frac{M}{V} - C_3'$

(2') $C_2' = \frac{M}{V} - nC_3'$

(3'') $C_3' = K_{eq}(nC_1C_2^{\,n-1}C_2' + C_1'C_2^{\,n})$

Applying (4), (1'), (2'), and (3'') become:

(1'') $C_1' = -\frac{M}{V}$

(2'') $C_2' = \frac{M}{V}$

(3''') $nC_1C_2' + C_1'C_2 = 0$

Substituting (1'') and 2'') into (3'''):

(5) $nC_1\frac{M}{V} - C_2\frac{M}{V} = 0$

Substituting (1) and (2) into (5):

(6) $n(V - x) - x = 0$

Solving (6) for n:

$$n = \frac{x}{V - x}$$

This result means that the determination of the volume ratio (and hence the mole ratio) of the components A and B which makes any relation of C_3 as a function of x a maximum or a minimum affords a calculation of n.

APPENDIX II

CONSTANCY OF THE STANDARD DINITROGEN TETROXIDE-IN-CHLOROFORM SOLUTIONS

In order to determine the effect of loss of dinitrogen tetroxide, through evaporation, on the concentration of the standard solutions, some quantitative determinations were made on these solutions after exposure to the air. Use was made of the disproportionation reaction which dinitrogen tetroxide undergoes in the presence of the hydroxide ion.

$$N_2O_4 + 2OH^- \rightleftharpoons NO_2^- + NO_3^- + H_2O$$

$$K_{eq} = 8 \times 10^{28} \text{ at } 27^\circ \quad (46)$$

Standard solutions of dinitrogen tetroxide of about 0.060 molar in chloroform were prepared. The solutions were exposed to the air for several minutes and then five milliliter aliquots withdrawn and titrated with standard sodium hydroxide solution. The titration was followed with a Beckmann, Model G pH Meter.

The results showed that maximum losses were such as to displace the actual volume ratios of the dielectric constant curves about 1.2 milliliters toward a higher proportion of the various sulfides. A shift in volume ratio of 1.2 milliliters would not greatly affect the mole ratio of sulfide to dinitrogen tetroxide at the maxima of the dielectric constant curves. The 1:1.5 ratio for di-n-butyl sulfide and di-isoamyl sulfide to dinitrogen tetroxide would become approxi-

mately 1:1.4. However, it is felt that this error represents an upper limit and does not reflect the actual losses encountered since great care was taken to see that the solutions were not exposed to the air any longer than was absolutely necessary.

APPENDIX III

ATTAINMENT OF TEMPERATURE EQUILIBRIUM BY SOLUTIONS IN THE DIELECTRIC CONSTANT MEASURING CELL

All physical constants are expressed in English units since a function which was determined graphically was expressed in these units (47).

The following assumptions were made:

1. The solutions are dilute enough to be treated as pure chloroform.
2. The conductivity of the thin glass measuring cell may be neglected.
3. Convection may be neglected.
4. The original temperature of the solution (just after mixing the pre-cooled separate dinitrogen tetroxide and sulfide solutions) is $-31^{\circ}F$.
5. Shaking the measuring cell containing the solution results in the solution assuming the average temperature between the temperature of the solution at its surface and the temperature at its center.
6. The effect of the nickel condenser plates may be neglected.

The solution was pre-cooled for three minutes at $-103^{\circ}F$, and then given twenty minutes at $-76^{\circ}F$ before taking the capacitance measurement.

The following symbols are used:

θ_c = temperature of solution at the center of the measuring cell.

θ_s = temperature of the solution at its surface.

θ_o = original uniform temperature of the solution.

θ_m = mean temperature of the solution.

k = mean therman conductivity of chloroform = 0.048Btu/hr ft^2 $^oF/ft$

C_p = mean heat capacity of chloroform = 0.41Btu/lb

ρ = mean density of chloroform = 89lb/ft^3

d = diameter of measuring cell = 0.104ft

$$\alpha = \frac{k}{\rho C_p} = \frac{0.048}{89 \times 0.41} = 0.00135$$

$f(\alpha, t, d^2)$ = a function of $\frac{\alpha t}{d^2}$ determined graphically.

The following relation holds for this situation:

$$\theta_c = \theta_s - (\theta_s - \theta_o) f(\alpha, t, d^2)$$

Pre-cooling period:

$\theta_s = -103^oF$

$\theta_o = -31^oF$

$t = \frac{3}{60} = \frac{1}{20}$ hr

$$\frac{\alpha t}{d^2} = \frac{0.00135}{20 \times 0.0108} = 0.0063$$

$f(\alpha, t, d^2) = 0.99$

$\theta_c = -103 - (-103 + 31)(0.99)$

$\theta_c = -32^oF$

$$\theta_m = \frac{\theta_c + \theta_s}{2} = \frac{-32 - 103}{2} = -67^oF$$

Twenty-minute period:

$$\theta_s = -76^\circ F$$

$$\theta_o = -67^\circ F$$

$$t = \frac{20}{60} = \frac{1}{3} \text{ hr}$$

$$\frac{\alpha t}{d^2} = \frac{0.00135}{3 \times 0.0108} = 0.0416$$

$$f(\alpha, t, d^2) = 0.45$$

$$\theta_c = -76 - (-76 + 67)(0.45)$$

$$\theta_c = -72^\circ F$$

$$\theta_m = \frac{-76 - 72}{2} = -74^\circ F$$

$$\theta_m = -59^\circ C$$

This calculation predicts that the temperature reached by the solution in the measuring cell is within one degree of the reported temperature (-60°). Assumptions 4 and 5 are very conservative and assumption 6 is reasonable since the heat capacity of a metal is relatively low. Assumption 1 is undoubtedly quite justified and assumptions 2 and 3 probably very nearly off-set one another. It is felt that on the basis of this calculation and from a few direct measurements, no doubt can exist that thermal equilibrium was attained.

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BIOGRAPHICAL SKETCH

Robert Dallas Whitaker was born on March 5, 1933, in Tampa, Florida. His undergraduate work was done at Washington and Lee University. He was graduated from this institution in 1955, with the degree of Bachelor of Science with special attainments in Chemistry. Following graduation from this institution, he spent one year at Yale University engaged in graduate study in the field of chemistry before going to the University of Florida to complete his graduate work. He expects to receive the degree of Doctor of Philosophy from the latter institution in August, 1959.

At Yale University and for his first year at the University of Florida, he was a graduate assistant. During his second year at the University of Florida, he was made a teaching assistant, and he was the holder of the du Pont Teaching Fellowship for the 1958-1959 school year.

He is a member of Phi Beta Kappa and Phi Eta Sigma. He is at present a student associate member in both Sigma Xi and the American Chemical Society.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 8, 1959

A H Gropp

Dean, College of Arts and Sciences

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